Organodisilanes: Synthesis, Stereochemistry and Mechanism(Dissertation_全文)

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KOHEI TAMAO

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PREFACE

The studies presented in this thesis have been carried out under the direction of Prof. Makoto Kumada at the Department of Synthetic Chemistry of Kyoto University during 1964 – 1970.

This thesis concerns synthesis, stereochemistry and mechanism of organodisilanes, especially silicon-containing heterocyclic compounds and (halomethyl)disilanes. The auther is convinced that the present studies will provide some significant information concerning the stereochemistry and mechanism of reactions at the silicon-silicon system which are the primary subjects in the chemistry of polysilanes.

The auther especially wishes to thank his honored teacher, Prof. Makoto Kumada, for his continuing guidance and helpful discussions throughout the course of the study. The auther's grateful thanks are also due to Assistant Prof. Mitsuo Ishikawa for his constant guidance and valuable discussions. He wishes to acknowledge the suggestions and criticisms of Prof. Hideki Sakurai (Tohoku University, Sendai), Drs. Keiji Yamamoto and Akira Hosomi. The auther wishes to express his appreciation to Prof. R. Fujishiro and Dr. K. Kimura at Osaka City University for the advice and help in the dipole moment measurements of compound (Ib) in Chapter 2. It is a pleasure to thank Messrs. K. Mimura, M. Matsuno, S. Sakamoto, T. Sugimoto, Y. Hiromoto and A. Noro for their active collaborations.

Finally, the auther is grateful to the parents for their constant encouragement.

KOHEI TAMAO

March 1971

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GENERAL INTRODUCTION

In recent years, considerable attention has been directed toward a study of the catenated linear and cyclic polysilanes[1-8]

Since Friedel and Ladenburg reported the synthesis of the first catenated organic derivative of silicon, *i. e.* hexaethyldisilane[9], the chemistry in this field had made but slow progress, especially because of a difficulty in getting the starting substance. The separation, by Kumada and his coworkers during 1952–1954[10], of methylchlorodisilanes, $Me_nSi_2Cl_{6-n}$, from the higher boiling fraction produced from the "direct synthesis" of methylchlorosilanes[11] has promoted the remarkable development of studies in the chemistry of polysilanes.

The majority of the studies on organopolysilanes has been, until recently, confined to the disilane derivatives. Work in the last few years, however, has indicated no experimental limit to the length or configuration of chains of silicon. Still, the chemistry of the organodisilanes holds an important position as a representative of the related reactions of the higher polysilanes. From the known range of compounds, it appears that silicon will form analogous configurations to carbon chains, with an important exception of an incapability of forming unsaturated compounds[12], but the polysilanes often behave in quite a different manner from the hydrocarbon counterparts in that they very easily undergo cleavage, disproportionation and intramolecular rearrangement of the silicon-silicon bond and that they exihibit characteristic ultraviolet absorptions[4,5,7,13] Also, the available *d* orbitals of silicon probably play an important role in many reactions at silicon[14-17]

The cleavage reactions which disilane systems undergo may be grouped in two categories: electrophilic and oxidative cleavage; and nucleophilic and reductive cleavage. The former involves cleavage of the silicon-silicon bond by halogens and by oxidating agents including perbenzoic acid, ozone and chromic acid. The cleavage of this type, in a certain sence, resemble the corresponding electrophilic addition reactions to the carbon-carbon double

bonds. The latter is exemplified by the reactions with alkali metals, organometallic reagents and alcoholic alkali.

It seems desirable to investigate these reactions at the silicon-silicon systems from stereochemical and mechanistic points of view. Accordingly, as the subject of study, we selected two types of organodisilane: (1) cyclic compounds containing a silicon-silicon bond and methylene linkages in the ring; and (2) halomethyl-substituted organodisilanes.

Whereas a vast number of rings containing carbon and silicon have been known and studied extensively[15-19], heterocyclic compounds containing the silicon-silicon bond and carbon atoms in their skeleton are few in number, and they were, until recently, merely synthesized. For the past decade, enthusiastic studies have been done concerning the stereochemistry of reactions at a silicon center by using optically active organosilicon compounds of various types[14,20,21] However, very little attention has been paid to the stereochemistry of compounds containing the silicon-silicon bond[22,23] In view of such circumstances we were primarily interested in the differences of reactivities between a strained silicon-silicon bond involved in moderate rings and a strain-free normal bond, and in the stereochemistry of geometrical isomers of heterocycles containing a silicon-silicon bond and a carbon chain where all the substituents on silicon are different. In Part 1, preparation, characterization and stereochemistry of mono-, di- and tri-cyclic systems of 1,2-disilacycloalkanes are described.

Also, in recent times there has been a considerable study of the synthesis and properties of organomonosilicon compounds with halogen atom(s) in the organic group attached to silicon[15,16,17,24] The current interest arises from the possibility of converting such compounds into high polymers with halogenated side groups[24] On the other hand, only a few reports have appeared concerning (halomethyl)disilanes and their chemistry seems promising. Part 2 deals with their reactions under nucleophilic and electrophilic conditions, especially from a mechanistic point of view.

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PART ONE

Silicon-containing Heterocyclic Compounds

CHAPTER ONE

PREPARATION AND REACTIONS OF 1,1,2,2-TETRAMETHYL-1,2-DISILACYCLOALKANES, FROM DISILACYCLOPENTANE TO DISILACYCLOOCTANE

SUMMARY

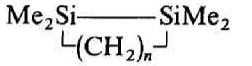
Four 1,2-disilacycloalkanes of the formula $Me_2\overline{SiSiMe_2-(CH_2)_n}$, where n equals 3, 4, 5 and 6, have been prepared by two methods: one involves reaction of $ClMe_2SiSiMe_2Cl$ with $BrMg(CH_2)_n MgBr$, the other comprises sodium/potassium condensation of $ClMe_2Si(CH_2)_nSiMe_2Cl$. It has been found that both the disilacyclo-pentane and -hexane exclusively undergo cleavage of the silicon-silicon bond when treated with concentrated sulfuric acid, whereas the disilacycloheptane gives several products in which the silicon-silicon bond has not been cleaved. The disilacyclopentane undergoes cleavage of the silicon-silicon bond when heated with 0.6 N sodium ethoxide in ethanol at 90°, while the disilacyclohexane is quite stable under the same conditions. The disilacyclopentane is oxidized with oxygen even at room temperature. Oxidation of the silacycloalkanes with bis (trimethylsilyl) peroxide is also described.

INTRODUCTION

Despite a large number of publications dealing with silacyclohydrocarbons[1], only very little interest has been shown in a class of compounds that contain the silicon-silicon bond in the ring.

We were primarily interested in preparing 1,1,2,2-tetramethyl-1,2-disilacycloalkanes and studying their chemical behavior, because the silicon-silicon bond in some of these compounds should be more highly strained and hence would be expected to be more reactive than, or different in modes of

reaction from, that in the related open-chain molecules. This chapter is concerned with the preparation of 1,1,2,2-tetramethyl-1,2-disilacyclopentane (I), -hexane (II), -heptane (III) and -octane (IV) and some of their reactions.



(I), $n = 3$

(II), $n = 4$

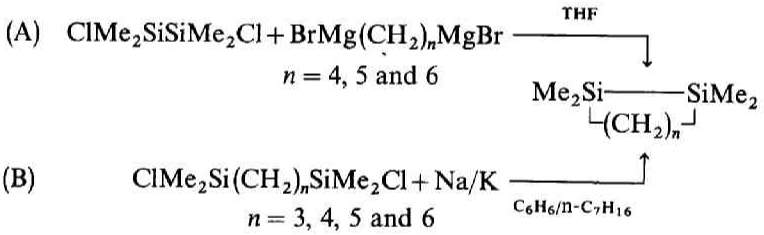
(III), $n = 5$

(IV), $n = 6$

RESULTS AND DISCUSSION

Synthesis

Two types of reaction were utilized to prepare the 1,2-disilacycloalkanes. Method (A) involves the reaction of di-Grignard reagents of the formula $BrMg(CH_2)_nMgBr$, n being 4, 5 and 6, with 1,2-dichlorotetramethyldisilane in tetrahydrofuran (THF), while method (B) entails the sodium/potassium condensation of α,ω-bis(chlorodimethylsilyl)alkanes of the formula $ClMe_2Si(CH_2)_nSiMe_2Cl$, where n equals 3 through 6, in benzene/n-heptane solution.



(A) $ClMe_2SiSiMe_2Cl + BrMg(CH_2)_nMgBr$ ($n = 4$, 5 and 6) —THF→ $Me_2Si(CH_2)_nSiMe_2$

(B) $ClMe_2Si(CH_2)_nSiMe_2Cl + Na/K$ ($n = 3$, 4, 5 and 6) —C_6H_6/n-C_7H_{16}→ $Me_2Si(CH_2)_nSiMe_2$

Yields of compounds (I)–(IV) obtained in typical runs by both methods are listed in Table 1, and some physical properties and analytical data in Table 2.

TABLE 1

SYNTHESIS OF 1,1,2,2-TETRAMETHYL-1,2-DISILACYCLOALKANES $Me_2Si(CH_2)_nSiMe_2$

Compound		*Preparative method*[a]	*Yield* (%)
No.	*n*		
(I)	3	(B)	45
(II)	4	(A)	66
		(B)	50
(III)	5	(A)	65
		(B)	18
(IV)	6	(A)	<3
		(B)	5

[a] See the text.

TABLE 2

SOME PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR 1,1,2,2-TETRAMETHYL-1,2-DISILACYCLOALKANES

Compound		*B.p.* (°C/mm)	n_D^{20}	d_4^{20}	*MR*	*C*(%)	*H*(%)
No.	*Formula*				*found* (*calcd.*)	*found* (*calcd.*)	*found* (*calcd.*)
(I)	$C_7H_{18}Si_2$	154–155	1.4708	0.8258	53.59 (53.77)	53.03 (53.08)	11.25 (11.46)
(II)	$C_8H_{20}Si_2$[a]	174	1.4722	0.8360	57.77 (58.12)	55.52 (55.72)	11.67 (11.69)
(III)	$C_9H_{22}Si_2$	76–77/16	1.4811	0.8473	62.90 (63.07)	58.06 (57.98)	11.64 (11.89)
(IV)	$C_{10}H_{24}Si_2$[b]	96/14	1.4882	0.8579	67.35 (67.71)	60.05 (59.91)	12.01 (12.07)

[a] *M.p.* −14 to −12°. [b] *M.p.* 7–9°.

Method (A) gave the disilacyclohexane (II) and -heptane (III) in good and comparable yields. However, this method was found to be far from satisfactory for synthesis of the disilacyclooctane (IV); sometimes only a trace of it could be detected by GLC in the reaction mixture. Almost all the product was a viscous polymeric material.

Method (B) afforded the disilacyclopentane (I) and -hexane (II) in satisfactory and approximately the same yield. While this method gave the disilacycloheptane (III) in much lower yield than did method (A), it gave a somewhat better yield of disilacyclooctane (IV).

As is well known (see *e.g.* ref. 2), the ease of cyclization of a chain

depends upon several factors, the most important among them being (*a*) an internal-angle strain of a ring to be formed, (*b*) the interactions between non-vicinal groups attached to the ring, and (*c*) the probability of intramolecular collision of the chain ends bearing the reactive groups. On these bases, the variation in yields obtained by method (B) with the ring size can be accounted for. Thus, a somewhat lower yield of the disilacyclopentane (I) as compared with the disilacyclohexane (II) may be attributed to somewhat larger ring strain inherent in the former, whereas the sharp drops in yield with increasing ring size from six through seven to eight are doubtless due to severely increasing repulsions of non-bonded groups attached to the ring, in addition to a lowering of the probability of intramolecular collision of the two reactive atoms at the chain ends. The conventional framework molecular model of the disilacyclooctane (IV) shown in Fig. 1 indicates that a great steric interaction is present among an axial methyl group and three axial hydrogen atoms on either side of the ring.

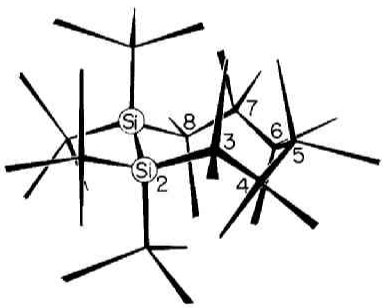


Fig. 1. A framework molecular model of 1,1,2,2-tetramethyl-1,2-disilacyclooctane.

TABLE 3

THE ^{1}H CHEMICAL SHIFTS OF 1,1,2,2-TETRAMETHYL-1,2-DISILACYCLOALKANES $Me_2Si(CH_2)_nSiMe_2$

Compound (*n*)	*Chemical shifts* (τ *values*)		
	Methyl	*Methylene* α *to silicon*	*Methylene* β *and* γ *to silicon*
3	9.88	9.25–9.45	8.1–8.6
4	9.95	9.1–9.5	8.3–8.6
5	9.95	9.1–9.6	8.3–8.5
6	9.97	9.1–9.3	8.3–8.8

The proton NMR spectral data, listed in Table 3, confirm the structure of each of the disilacycloalkanes.

Reactions with concentrated sulfuric acid

Much work has been done on the demethylation by concentrated sulfuric acid of compounds containing certain trimethylsilyl organic structures[3] Kumada *et al.* reported[4] that this process was successfully applied to hexamethyldisilane without being accompanied by significant cleavage of its silicon-silicon bond to give, after treatment with ammonium chloride or fluoride, compounds of the formula $XMe_2SiSiMe_2X$, where X stands for Cl or F, in satisfactory yields. However, 1,1-dimethyl-1-silacyclobutane[5], -pentane[6] and -hexane[7] were reported to undergo the ring opening either exclusively or predominantly rather than the demethylation when treated with concentrated sulfuric acid. It was therefore of considerable interest to examine the behavior of the disilacycloalkanes toward the action of sulfuric acid.

The products obtained from reaction of compounds (I), (II) and (III) with 98% sulfuric acid at a temperature of 17–35° followed by treatment with ammonium hydrogen fluoride were analyzed by gas chromatography. It was found that the first two compounds (I) and (II) violently reacted with sulfuric acid at 17–20° and exclusively underwent cleavage of the silicon-silicon bond to give α,ω-bis(fluorodimethylsilyl)propane and -butane, respectively, in very high yields.

$$Me_2Si\underset{\llcorner(CH_2)_n\lrcorner}{\text{———}}SiMe_2 \xrightarrow[2.\ NH_4F\cdot HF]{1.\ H_2SO_4} FMe_2Si(CH_2)_nSiMe_2F$$

(I) $n=3$; (II) $n=4$

On the other hand, reaction of the disilacycloheptane (III) with sulfuric acid was not so vigorous as that of (I) and (II), and gave several products. The reaction that was carried out at a lower temperature (17–18°) and discontinued when the reaction mixture had just become homogeneous gave, after treatment in the usual way with ammonium hydrogen fluoride, two compounds in the ratio of about 1 : 1 as the main products: 1-fluoro-2-n-pentyltetramethyldisilane (V) and 1-fluoro-1,2,2-trimethyl-1,2-disilacycloheptane (VI) (see Fig. 2a). These two new products were isolated in a reasonably

pure state by preparative GLC. An authentic sample of (V) was prepared in 60% yield by the reaction of n-pentylmagnesium chloride with 1,2-difluorotetramethyldisilane* Further proof for structures of (V) and (VI) was afforded by their conversion to n-pentylpentamethyldisilane (VII) and compound (III), respectively, through the reaction with methylmagnesium bromide.

$(n\text{-}C_5H_{11})Me_2SiSiMe_2F$ (V) $Me_2Si(CH_2)_5SiMeF$ (VI) $(n\text{-}C_5H_{11})Me_2SiSiMe_3$ (VII)

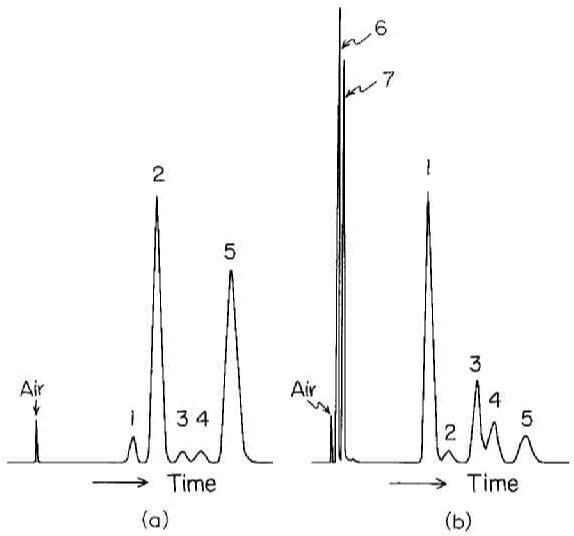


Fig. 2. Gas chromatograms of the products from reaction of 1,1,2,2-tetramethyl-1,2-disilacycloheptane (III) with H_2SO_4 followed by treatment with $NH_4F \cdot HF$. (a) Reaction at 17–18°. (b) Reaction at 17–35°.
(1), $F(n\text{-}C_5H_{11})MeSiSiMe_2F$ (VIII); (2), $(n\text{-}C_5H_{11})Me_2SiSiMe_2F$ (V); (3), $FMeSiSiMeF(CH_2)_5$ (IX); (4), $FMe_2Si(CH_2)_5SiMe_2F$ (X); (5), $Me_2SiSiMeF(CH_2)_5$ (VI) (6) $FMe_2SiSiMeF_2$ (XII); (7), $FMe_2SiSiMe_2F$ (XI).

In addition to the two principal products, the formation of insignificant quantities of 1,2-difluoro-1-n-pentyltrimethyldisilane (VIII), 1,2-difluoro-1,2-dimethyl-1,2-disilacycloheptane (IX) and 1,5-bis(fluorodimethylsilyl)pentane (X) were observed by GLC. No starting substance was detected.

$F(n\text{-}C_5H_{11})MeSiSiMe_2F$ (VIII) $FMeSi(CH_2)_5SiMeF$ (IX) $FMe_2Si(CH_2)_5SiMe_2F$ (X)

*Use of n-pentylmagnesium *bromide* instead of choride gave rise to the formation of considerable amounts of 1-bromo-2-n-pentyltetramethyldisilane (see Experimental).

An authentic sample of compound (VIII) was obtained from the higher temperature reaction that will be described below, while that of compound (X) was prepared according to the reported procedure[8] The identification of compound (IX) was also based on the complete coincidence of its retention time on GLC with that of one of the *cis, trans* isomers of 1,2-difluoro-1,2-dimethyl-1,2-disilacycloheptane that was prepared by fluorodephenylation of 1,2-diphenyl-1,2-dimethyl-1,2-disilacycloheptane with sulfuric acid and ammonium hydrogen fluoride in the cold.

When the reaction was initially carried out by keeping the temperature at 17–18°, later by increasing it gradually up to 35° and holding it at this temperature until gas evolution ceased, the composition of the product mixture was substantially altered. The gas chromatogram reproduced in Fig. 2b indicates that at the cost of a sharp decrease in quantities of the two major products (V) and (VI) in the lower temperature reaction, yields of the two (VIII) and (IX) of the three compounds that had been minor were increased and also a few other new lower-boiling compounds were formed. In contrast, an increase in yield of compound (X) was insignificant. From this product mixture we could isolate, by preparative GLC, both 1,2-difluoro-1-n-pentyltrimethyldisilane (VIII) and 1,2-difluorotetramethyldisilane (XI) in the pure state, and 1,1,2-trifluorotrimethyldisilane (XII) in a somewhat impure state.

$FMe_2SiSiMe_2F$ (XI) $F_2MeSiSiMe_2F$ (XII)

As can be seen from Table 4, which summarizes the yields of the

TABLE 4

CLEAVAGE OF THE SILICON–SILICON BOND IN 1,1,2,2-TETRAMETHYL-1,2-DISILACYCLOALKANES BY SULFURIC ACID

No. of compound	*Reaction temp.* (°C)	*Cleavage*[a] (%)
(I)	18–20	>90
(II)	18–20	>90
(III)	17–18	< 7
	17–35	< 7

[a] Estimated by gas chromatographical analysis of the products formed on treatment with ammonium hydrogen fluoride.

silicon-silicon cleavage products from the action of sulfuric acid on compounds (I) – (III), the silicon-silicon bond in the 1,2-disilacycloheptane (III) is as stable as that in hexamethyldisilane toward concentrated sulfuric acid. On the other hand, this bond, in the lower members of the homologous series, (I) and (II), is extraordinarily susceptible to cleavage by the action of sulfuric acid. Probably, in these smaller ring molecules, an internal-angular strain may be concentrated at the silicon-silicon bond, whereas in molecules with a suitably large ring size, for example, compound (III), the strain will be smaller and uniformly distributed all over the ring. In the latter case, therefore, cleavage by sulfuric acid will occur at the silicon-carbon bond according to a mechanism accepted for electrophilic substitutions at a saturated carbon[9]

Reaction with sodium ethoxide in ethanol

Hexaorganodisilanes have long been known to be resistant to alcoholic alkali[10-12] We have reconfirmed this fact by observing that ethylpentamethyldisilane underwent no change at all after having been refluxed in 0.6 *N* ethanolic solution of sodium ethoxide for many hours.

As regards the behavior of 1,1-dimethyl-1-silacycloalkanes toward alcoholic alkali, the silacyclobutane has been reported by Sommer and Baum[5] to undergo ring opening with considerable heat evolution when treated with 1 *N* potassium hydroxide in ethanol at room temperature.

We, therefore, were much interested to learn how the 1,2-disilacycloalkanes would behave toward this type of reagents, and we found that compound (I) underwent cleavage exclusively at the silicon-silicon bond with evolution of an almost quantitative volume of hydrogen when heated at 90° with 0.6 *N* sodium ethoxide in ethanol over an 80-h period, giving 1,3-bis(ethoxydimethylsilyl)propane (XIII) and 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane (XIV), together with a small amount of higher-boiling substance.

$$Me_2Si\overset{\llcorner(CH_2)_3\lrcorner}{\text{———}}SiMe_2 \xrightarrow[90°]{EtONa/EtOH}$$

$$(EtO)Me_2Si(CH_2)_3SiMe_2(OEt) + Me_2Si\overset{\llcorner(CH_2)_3\lrcorner}{—}O—SiMe_2 + H_2$$

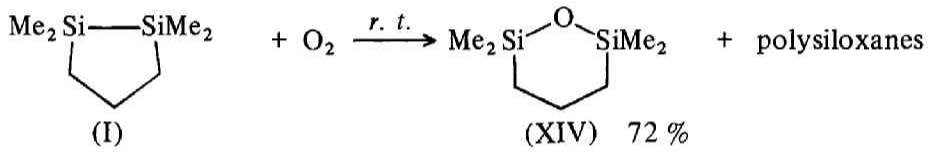
(XIII) (XIV)

In marked contrast, the disilacyclohexane (II) did not react at all with sodium ethoxide in ethanol under the same conditions as above.

These results indicate that the disilacyclopentane (I) is much more highly strained than the disilacyclohexane (II).

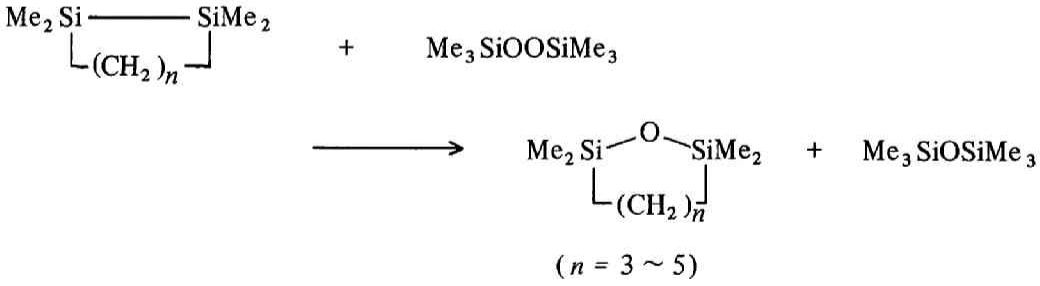
Oxidation with oxygen and bis(trimethylsilyl) peroxide

Although the silicon-silicon bond has been considered to be stable to air[13], the five membered ring (I) was relatively easily oxidized in air and contaminated with substantial amounts of siloxanes. When oxygen was passed through the neat liquid at room temperature, (I) immediately absorbed oxygen exothermally to form the corresponding cyclic siloxane (XIV) in 72 % yield, leaving nonvolatile polysiloxanes. The higher homolog (II) was little affected



(I) (XIV) 72 %

with oxygen under similar conditions. In connection with the aerobic oxidation, we investigated the oxidation of (I) – (IV) with bis(trimethylsilyl) peroxide[14] The results are summarized in Table 5. Products were the corresponding cyclic siloxane and hexamethyldisiloxane having arisen from the peroxide.



(n = 3 ~ 5)

Here again the disilacyclopentane (I) was much more reactive than the higher homologs (II) and (III) and the disilacyclooctane (IV) did not react with the peroxide under similar conditions.

TABLE 5

Reaction with Bis(trimethylsilyl) peroxide (BSPO)

Compound No.	mmole	BSPO mmole	Conditions °C	Time (h)	Product	Yield(%)[a]
$Me_2Si(CH_2)_nSiMe_2$					$Me_2Si(CH_2)_nOSiMe_2$	
n = 3 (I)	0.616	1.23	*r. t.*	1.5	n = 3	95.0
n = 4 (II)	0.190	0.561	80	16	n = 4	98.4
n = 5 (III)	1.47	2.49	80	45	n = 5	64.4
n = 6 (IV)	0.943	1.65	80	45	Not reacted	

[a]Estimated by GLC.

EXPERIMENTAL

All organosilicon compounds described here were fractionally distilled through a 1.0 x 30 cm column packed with glass helices, and were gas chromatographically homogeneous, unless otherwise stated. Boiling points were uncorrected. NMR spectra were obtained in carbon tetrachloride solutions containing cyclohexane as an internal reference (Varian A-60, 60 Mc/sec).

1,2-Dichlorotetramethyldisilane was most conveniently prepared by chlorodemethylation of hexamethyldisilane with acetyl chloride in the presence of anhydrous aluminum chloride, as reported recently[15]

1,3-Bis(chlorodimethylsilyl)propane, 1,4-bis(chlorodimethylsilyl)butane, 1,5-bis(chlorodimethylsilyl)hexane were prepared by heating the corresponding α,ω-bis(fluorodimethylsilyl)-alkanes[8] with excess trimethylchlorosilane in the presence of anhydrous aluminum chloride[16] in a distillation apparatus fitted with the same column as described above, and by removing trimethylfluorosilane as it was formed. After no appreciable reaction

occurred (about 20 h), the residue was flash-distilled *in vacuo*, and the catalyst-free distillate was redistilled in the column. Table 6 lists some physical properties, yields and analytical data for the α,ω-bis(chlorodimethylsilyl)alkanes obtained.

1,1,2,2-Tetramethyl-1,2-disilacyclopentane (I)

Method (B). An alloy was prepared from 6.0 g (0.26 g-atom) of sodium and 51 g (1.3 g-atom) of potassium in 150 ml of n-heptane. To the stirred mixture was added dropwise 150 g (0.65 mole) of 1,3-bis(chlorodimethylsilyl)propane diluted with 700 ml of benzene under gentle reflux over a 3-h period. The reaction mixture was then kept under reflux for an additional 30 h with stirring. At this point it was decomposed in the cold by adding successively 200 ml of an ethanol/acetic acid mixture (1 : 1), 400 ml of absolute ethanol, 200 ml of 50% aqueous ethanol and 800 ml of water. The organic layer was separated, combined with ether extracts from the aqueous phase, washed with sodium bicarbonate solution to neutral, dried over calcium chloride and distilled initially through a Widmer column for the purpose of removing most of the solvents but later in the packed column to give 74 g of a fraction boiling over the range of 149–154° and 38 g of residue. Since the distillate was found to contain a relatively large amount of a siloxane derivative, it was treated with sulfuric acid in the cold. The acid-insoluble upper layer was separated, washed to neutral, dried and finally redistilled to give 47 g (45 % yield) of compound (I), b.p. 154–155°, in the pure state.

1,1,2,2-Tetramethyl-1,2-disilacyclohexane (II)

Method (A). In a 500-ml three-necked flask there was prepared in the usual way a Grignard solution from 58 g (0.27 mole) of 1,4-dibromobutane and 13 g (0.52 g-atom) of magnesium in 250 ml of tetrahydrofuran (THF). To the stirred solution was added dropwise and with cooling 40 g (0.21 mole) of 1,2-dichlorotetramethyldisilane diluted with

TABLE 6

SOME PHYSICAL PROPERTIES, YIELDS AND ANALYTICAL DATA FOR $ClMe_2Si(CH_2)_nSiMe_2Cl$

n	*b.p.* (°C/*mm*)	n_D^{20}	d_4^{20}	*MR found* (*calcd.*)	*Yield* (%)	*C* (%) *found* (*calcd.*)	*H* (%) *found* (*calcd.*)	*Cl* (%) *found* (*calcd.*)
3[a]	103–104/21	1.4497	0.9878	62.35 (62.10)	89	36.80 (36.66)	8.09 (7.91)	30.47 (30.93)
4[b]	123–124/24	1.4509	0.9782	66.70 (66.75)	78	39.32 (39.49)	8.32 (8.28)	29.05 (29.14)
5	132–133/21	1.4537	0.9813	70.98 (71.09)	78	42.17 (42.00)	8.68 (8.62)	27.69 (27.55)
6[c]	113–116/3	1.4538	0.9613	76.42 (76.04)	75	44.36 (44.26)	9.06 (8.91)	25.80 (26.13)

[a] Reported[17]: b.p. 118–119°/41 mm, n_D^{20} 1.4474, d_4^{20} 0.9855. [b] Reported[18]: b.p. 112°/15 mm [c] Reported[19]: b.p. 110°/2 mm.

100 ml of THF over a 15 min period. The mixture was then refluxed for 6 h with continuous stirring. At this point, about 150 ml of THF was distilled off from the mixture, and the residue was decomposed with saturated solution of ammonium chloride. The resulting organic layer and ether extracts from the aqueous phase were combined, washed with water, dried over potassium carbonate, and distilled to give 21 g of a liquid boiling over the range of 70–110°/30 mm and 13 g of residue. Redistillation of the distillate through the column gave 19 g (52 % yield) of compound (II) in the pure state.

A second run was carried out by using about 2.5 times as large quantities of materials as before and in essentially the same way but by spending 2 h in addition of the chlorosilane. The yield of compound (II) was increased to 66 %.

Method (B). 1,4-Bis(chlorodimethylsilyl)butane (36.5 g, 0.15 mole) diluted with 200 ml of benzene was allowed to react with sodium (2.3 g, 0.10 g-atom)/potassium (11.7 g, 0.30 g-atom) alloy dispersed in 50 ml of n-heptane. The reaction mixture was worked up in the same manner as described in the preparation of compound (I) to give 13 g (50 % yield) of compound (II) which was slightly contaminated by a siloxane compound.

1,1,2,2-Tetramethyl-1,2-disilacycloheptane (III)

Method (A). To a Grignard solution prepared from 157 g (0.68 mole) of 1,5-dibromopentane and 32 g (1.32 g-atom) of magnesium in 500 ml of THF was added 102 g (0.545 mole) of 1,2-dichlorotetramethyldisilane diluted with 200 ml of THF over a 50-min period. After a work-up similar to that described in the preparation of compound (II), there was obtained 42 g (41 % yield) of compound (III) in the pure state. A second run carried out by using identical quantities of materials but by spending 3 h in addition of the chlorosilane gave compound (III) in 65 % yield.

Method (B). The procedures and quantities of materials used were the same as those for the preparation of compound (II) except that 38.5 g (0.15 mole) of 1,5-bis-(chlorodimethylsilyl)pentane was employed in place of 1,4-bis(chlorodimethylsilyl)butane. There was obtained 5 g (18% yield) of compound (III), along with 18 g of residue. In a second run, to an alloy prepared from 0.6 g (0.025 g-atom) of sodium and 5.3 g (0.14 g-atom) of potassium in 20 ml of n-heptane was added 16 g (0.062 mole) of 1,5-bis(chlorodimethylsilyl)pentane diluted with 650 ml of benzene under gentle reflux with vigorous stirring over an 18-h period. After the addition was completed, the mixture was refluxed with stirring for an additional 40 h. It was then worked up as above to give 3.2 g of impure compound (III) Its purity was estimated as about 70 % by GLC, hence the yield corresponded to 19 %. Residue weighed 9.5 g. The results of these two runs thus indicate that method (B) is unfavorable for synthesis of compound (III), regardless the extent of dilution.

1,1,2,2-Tetramethyl-1,2-disilacyclooctane (IV)

Method (A). To a Grignard solution prepared from 24.5 g (0.1 mole) of 1,6-dibromohexane and 4.9 g (0.2 g-atom) of magnesium in 300 ml of THF was added 19 g (0.1 mole) of 1,2-dichlorotetramethyldisilane diluted with 500 ml of THF over an 8.5-h period. After 16-h reflux and then a work-up in the usual way, 1.3 g of a distillate boiling over the range of 70–130°/25 mm was obtained, along with 18 g of residue. GLC analysis indicated that the distillate contained about 0.6 g (3 % yield) of compound (IV).

Method (B). To an alloy prepared from 0.9 g (0.04 g-atom) of sodium and 8.2 g (0.21 g-atom) of potassium in 70 ml of n-heptane was added a solution of 27.1 g (0.10 mole) of 1,6-bis(chlorodimethylsilyl)hexane in 1.2 l of benzene under gentle reflux with stirring over a 30-h period. The reaction mixture was heated to reflux for an additional 30 h, and then worked up as described in the preparation of compound (I) Distillation of the resulting organic layer gave 2.5 g of a fraction boiling over the range of 80–143°/10 mm and 18 g of residue. Five runs were carried out under the same conditions. All the distillates were combined and treated with 150 g of concentrated sulfuric acid at 4° for the purpose of removing a slight amount of any silicon–hydrogen compound (detected by IR). The acid-insoluble layer was washed, dried and distilled to give 5.0 g (5 % yield) of compound (IV) in the pure state.

Reaction of (I) with H_2SO_4

The techniques for reaction of 1,2-disilacycloalkanes (I) – (III) with concentrated sulfuric acid followed by treatment with ammonium hydrogen fluoride were essentially the same as described previously by Kumada *et al.*[4]

A mixture of 30 g (0.19 mole) of compound (I) and 240 g of concentrated sulfuric acid was stirred vigorously at 18–20° Gas evolution took place rapidly and ceased when approximately equimolar amount of the gas was collected (*ca.* 30 min) and the reaction mixture became homogeneous. The mixture was then treated with 31 g (0.54 mole) of ammonium hydrogen fluoride in the cold. The resulting organic layer (34.5 g, 90 % yield) was found to be homogeneous by GLC. Distillation gave 33.5 g of 1,3-bis(fluorodimethylsilyl)propane, b.p. 61°/26 mm, n_D^{20} 1.3931, d_4^{20} 0.9147, *MR* 51.25 (calcd. 51.28); reported[8] b.p. 156°, n_D^{20} 1.3926, d_4^{20} 0.9147. (Found: F, 19.46. $C_7H_{18}F_2Si_2$ calcd.: F, 19.35%.)

Reaction of (II) with H_2SO_4

The reaction of 28 g (0.16 mole) of compound (II) with 200 g of concentrated sulfuric acid at 18–20°, followed by treatment with 26 g (0.46 mole) of ammonium hydrogen fluoride gave 29 g (90 % yield) of 1,4-bis(fluorodimethylsilyl)butane, b.p. 176°, n_D^{20} 1.3984, d_4^{20} 0.9095, *MR* 55.89 (calcd. 55.93); reported[18] b.p. 176° (Found: F, 17.71. $C_8H_{20}F_2Si_2$ calcd.:F, 18.06 %.) A negative result to the bromine test on the sample

indicated complete disappearance of the silicon–silicon bond.

1-Fluoro-2-n-pentyltetramethyldisilane (V) and 1-bromo-2-n-pentyltetramethyldisilane

(a) From n-pentylmagnesium chloride. To a stirred mixture of 15.4 g (0.10 mole) of 1,2-difluorotetramethyldisilane diluted with 20 ml of ether was gradually added with cooling a solution of n-pentylmagnesium chloride, prepared from 14.8 g (0.14 mole) of n-pentyl chloride and 2.9 g (0.12 g-atom) of magnesium in 80 ml of ether. After being stirred at room temperature for 4 h and then heated to reflux for 5 h, the mixture was filtered. Fractional distillation of the filtrate gave 12.5 g (60 % yield) of 1-fluoro-2-n-pentyltetramethyldisilane, b.p. 67°/15 mm, n_D^{20} 1.4278, d_4^{20} 0.8341, *MR* 63.66 (calcd. 63.67). (Found: F, 9.11. $C_9H_{23}FSi_2$ calcd.: F, 9.20 %.)

(b) From n-pentylmagnesium bromide. A second run was carried out in essentially the same way and by using identical quantities of materials except for use of n-pentyl bromide (18.1 g, 0.12 mole) in place of the chloride. Fractionation gave 4.0 g (19 % yield) of about 97 % pure 1-fluoro-2-n-pentyltetramethyldisilane (V) and 12.5 g (47 % yield) of 1-bromo-2-n-pentyltetramethyldisilane, b.p. 110°/24 mm, n_D^{20} 1.4725, d_4^{20} 1.0342, *MR* 72.46 (calcd. 72.30). (Found: Br, 29.92. $C_9H_{23}BrSi_2$ calcd: Br, 29.89 %)

Reaction of (III) with H_2SO_4

(a) At 17–18° A mixture of 18.6 g (0.10 mole) of compound (III) and 128 g of concentrated sulfuric acid was stirred at 17–18° When gas evolution (*ca.* 2 l) ceased, the mixture became completely homogeneous. It was treated with 19 g (0.33 mole) of ammonium hydrogen fluoride in the cold. The resulting organic layer (19 g) was separated and distilled to give 0.8 g of a lower-boiling material and 16 g of a fraction boiling over the range of 70–88°/25 mm, which was found to consist of two major products and three minor ones by GLC analysis (see Fig. 2a). One of the major products was isolated by preparative GLC (column, Silicone-DC 550; temperature, 132°; He velocity, 30 cc/min) and identified as 1-fluoro-2-n-pentyltetramethyldisilane (V), while another major product was also isolated by GLC and identified as about 90 % pure 1-fluoro-1,2,2-trimethyl-1,2-disilacycloheptane (VI), n_D^{20} 1.4627, d_4^{20} 0.9331, *MR* 56.18 (calcd. 56.97). (Found: C, 49.47; H, 10.31; F, 10.46. $C_8H_{19}FSi_2$ calcd.: C, 49.54; H, 10.06; F, 9.98 %.) Samples of both compounds reacted with bromine violently in the cold, which affords evidence for the presence of the silicon–silicon bond.

Further evidence for the structure of (V) and (VI) was obtained as follows. To 8 g (Found: F, *ca.* 10 %) of the fraction boiling at 70–88°/25 mm was added 0.09 mole of methylmagnesium bromide in 70 ml of ether. The mixture was then heated over a 32-h period. Hydrolysis followed by distillation gave 7 g of a liquid boiling over the range of 100–105°/36 mm, and consisting of two principal components in the ratio of *ca.* 1:1 and one component in an insignificant quantity. The first two products could be isolated in the reasonably pure state by GLC. One was identified as n-pentylpenta-

methyldisilane (VII), n_D^{20} 1.4442, d_4^{20} 0.7705, *MR* 69.77. (calcd. 69.47) (Found: C, 59.23; H, 12.79. $C_{10}H_{26}Si_2$ calcd.: C, 59.31; H, 12.94 %), and the other as compound (III) by GLC and IR spectroscopic analyses. The last minor product proved to be 1,5-bis-(trimethylsilyl)pentane.

(b) At 17–35° A mixture of the same quantities of materials was stirred vigorously at 17–18° as described in *(a)*. Since when 2 l of gas was evolved the reaction appeared not to proceed further, the reaction temperature was increased gradually to 35° and maintained there. Gas evolution took place until about 3.3 l of gas was collected. At this point the reaction mixture was treated with 19 g (0.33 mole) of ammonium hydrogen fluoride and worked up in the usual way, giving 18.5 g of an organic layer. Its gas chromatogram is reproduced in Fig. 2b. Simple distillation gave two fractions: (1), 3.0 g, boiling over the range of 65–110° and (2), 12.5 g, boiling mostly at 172–184° Fraction (1) consisted mainly of two compounds in the ratio of about 1:1. Preparative GLC gave 1,1,2-trifluorotrimethyldisilane (XII) in an impure state (Found: F, 33.85. $C_3H_9F_3Si_2$ calcd.: F, 36.01 %.) and 1,2–difluorotetramethyldisilane (XI) in the pure state, its retention time in the gas chromatogram being superimposable with that of an authentic sample[4] (Found: F, 24.38. $C_4H_{12}F_2Si_2$ calcd.: F, 24.62 %.) Both compounds reacted with bromine energetically. Fraction (2) was composed of five compounds, from which we could isolate 1,2-difluoro-1-n-pentyltrimethyldisilane (VIII), b.p. 59–60°/18 mm, n_D^{20} 1.4113, d_4^{20} 0.9128, *MR* 57.27 (calcd. 58.07). (Found: F, 17.91. $C_8H_{20}F_2Si_2$ calcd.: F, 18.06 %.) Other four products were identified by GLC as shown in Fig. 2b.
A colorless liquid (0.5 g) was collected during the reaction in a Dry Ice/acetone trap connected to the reaction flask *via* the reflux condenser. It was identified as n-pentane.

1,2-Diphenyl-1,2-dimethyl-1,2-disilacycloheptane

To a Grignard solution, prepared from 20.2 g (0.087 mole) of 1,5-dibromopentane and 3.4 g (0.14 g-atom) of magnesium in 130 ml of THF, was added 19 g (0.061 mole) of 1,2-dimethyl-1,2-diphenyl-1,2-dichlorodisilane (see Chapter 2) diluted with 20 ml of THF over a period of 1 h. After standing overnight, the reaction mixture was heated to reflux for 10 h and then about 100 ml of THF was removed by distillation. The residue was then refluxed for additional 7 h, and hydrolyzed with saturated aqueous solution of ammonium chloride. The organic layer and ether extracts (*ca.* 300 ml) were combined, washed with water and dried over calcium chloride. After removal of the solvents, distillation gave 13 g of a liquid boiling over the range of 50 –185°/3 mm, along with 4.5 g of residue. Fractionation afforded 7.0 g (37% yield) of 1,2-diphenyl-1,2-dimethyl-1,2-disilacycloheptane as a *cis/trans* mixture, b.p. 180–184°/4 mm, n_D^{20} 1.5884, d_4^{20} 1.0164, MR_D 102.90 (calcd. 103.19). (Found: C, 73.34; H, 8.60. $C_{19}H_{26}Si_2$ calcd.: C, 73.47; H, 8.44 %.)

1,2-Difluoro-1,2-dimethyl-1,2-disilacycloheptane

To 18 g of concentrated sulfuric acid was added 5.0 g (0.016 mole) of 1,2-diphenyl-1,2-dimethyl-1,2-disilacycloheptane with vigorous stirring, under cooling in an ice bath, to maintain the reaction temperature below 5° No gas evolution was observed during the reaction. After 3.5 h-stirring, 4 g (0.07 mole) of ammonium hydrogen fluoride was added in three portions with cooling. The resulting organic layer and benzene extracts from the acid layer were combined and distilled to give 2.5 g (crude, 81 % yield) of a liquid boiling over the range of 68 –86°/30 mm (mainly 83°/30 mm), consisting of two components, possibly the *cis* and *trans* isomers, n_D^{20} 1.4518, d_4^{20} 1.0331, MR_D 50.74 (calcd. 51.17). (Found: C, 43.05; H, 8.73; F, 19.35. $C_7H_{16}F_2Si_2$ calcd.: C, 43.25; H, 8.30; F, 19.55 %.)

Reaction of (I) with EtONa/EtOH

In a 100-ml Erlenmeyer flask fitted with a reflux condenser that was connected to an apparatus for collecting gas was placed a mixture of 4.8 g (0.03 mole) of compound (I) and 10 ml of 0.6 *N* sodium ethoxide in ethanol. The mixture was maintained at a temperature of 90 ± 5° by means of a silicone-oil thermostat and agitated vigorously with a magnetically operated stirrer. After 80-h reaction, 0.63 l (*ca.* 90 % of theory) of hydrogen was collected and only a trace of the starting substance (I) was detected by GLC. Distillation of the flask content under reduced pressure gave the following three fractions: (1) 0.5 g, b.p. 55–116°/33 mm, consisting of *ca.* 20 % of 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane (XIV) and *ca.* 80 % of 1,3-bis(ethoxydimethylsilyl)propane (XIII) ; (2) 2.8 g of compound (XIII), b.p. 118°/33 mm, n_D^{20} 1.4231, d_4^{20} 0.8555, *MR* 73.98 (calcd. 73.91) (Found: C, 53.37; H, 11.49. $C_{11}H_{28}O_2Si_2$ calcd.: C, 53.16; H, 11.36 %.) and (3) 0.7 g, boiling over the range of 80–120°/2 mm, n_D^{20} 1.4422, d_4^{20} 0.8832, and being almost homogeneous by GLC.

Attempted reaction of (II) with EtONa/EtOH

A similar reaction to that above with the exception of use of 5.2 g (0.03 mole) of compound (II) in place of compound (I) was attempted. However, no gas evolution occurred after 75 h, and all the starting substance was recovered unchanged.

Ethylpentamethyldisilane

To 0.08 mole of ethylmagnesium bromide in 100 ml of ether was added 11.7 g (0.07 mole) of chloropentamethyldisilane[4] After a work-up in the usual way, 6.0 g (54 % yield) of ethylpentamethyldisilane, b.p. 137–138°, n_D^{20} 1.4361, d_4^{20} 0.7512, *MR* 55.85 (calcd. 55.83) was obtained. (Found: C, 52.93; H, 12.64. $C_7H_{20}Si_2$ calcd.: C, 52.41: H, 12.57 %.)

Attempted reaction of ethylpentamethyldisilane with EtONa/EtOH

A mixture of 3.2 g (0.02 mole) of $EtMe_2SiSiMe_3$ and 6.7 ml of 0.6 *N* EtONa in ethanol was stirred under the same conditions as above. No gas evolution was observed at all, and GLC analysis revealed that no compounds were present other than the starting substance.

Oxidation of (I) with oxygen

Oxygen was bubbled through 3.2 g (20 mmole) of (I) at room temperature. Exothermal absorption of oxygen was immediately observed. After 328 ml (at STP, 14.7 mmole) of absorption (8.5 h), GLC analysis of the reaction mixture showed that the starting material was no longer present. The mixture remained clear, but had a pungent odor and contained a small amount of an insoluble liquid, possibly water. Distillation gave 2.5 g (72 % yield) of 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane (XIV), b.p. 38-39°/16 mm, along with 0.5 g of residue. The retention time on GLC and IR spectrum having ν(Si—O) at 987 cm^{-1} are exactly coincident with those of an authentic sample[20] (Found: C, 48.07; H, 10.52. $C_7H_{18}OSi_2$ calcd.: C, 48.21; H, 10.40%.)

Oxidation of (II) with oxygen

Similarly, 3.0 g of (II) was allowed to react with oxygen at 40–45° After 60 h, only 55 ml of oxygen was absorbed and a trace of the corresponding siloxane was detected by GLC.

Oxidation with bis(trimethylsilyl) peroxide

Bis(trimethylsilyl) peroxide was prepared in essentially the same manner as given in the literature[14] The reaction was carried out in a small glass sealed tube. The reaction conditions, products and yields are listed in Table 5. Products from (I), (II) and (III) were, respectively, 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane (XIV)[20], 2,2,7,7-tetramethyl-1-oxa-2,7-disilacycloheptane, having n_D^{20} 1.4350, d_4^{20} 0.8859 (lit.[18] n_D^{20} 1.4340, d_4^{20} 0.8794) and ν(Si—O) at 1020 cm^{-1}, (Found: C, 50.77; H, 10.55. $C_8H_{20}OSi_2$ calcd.: C, 50.99; H, 10.70 %.), and 2,2,8,8-tetramethyl-1-oxa-2,8-disilacyclooctane, having ν(Si—O) at 1040 cm^{-1} (Found: C, 53.62; H, 11.01. $C_9H_{22}OSi_2$ calcd.: C, 53.39; H, 10.92 %.)

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CHAPTER TWO

PREPARATION, CHARACTERIZATION AND STEREOCHEMISTRY OF *cis*- AND *trans*-1,2-DISUBSTITUTED-1,2-DIMETHYL-1,2-DISILACYCLOHEXANES

SUMMARY

cis- and *trans*-1,2-Diphenyl-1,2-dimethyl-1,2-disilacyclohexane (Ia) and the 1,2-bis(*p*-chlorophenyl) analogs (Ib) have been prepared. The assignment of geometrical configuration for a pair of isomers of (Ib) has been achieved on the basis of dipole moment data, and that for isomers of (Ia) has been by correlating them with the isomers of (Ib) by reducing the latter to the former with the asymmetric silicon center intact. Fluorodephenylation of (Ia) by treatment with sulfuric acid and ammonium hydrogen fluoride always gives a 1 : 1.9 mixture of *cis*- and *trans*-1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane (IIa) regardless of whether the *cis* or the *trans* isomer of (Ia) or a mixture of both is employed. The geometrical configuration of these isomers has been determined by converting them into (Ia). Chlorodephenylation of (Ia) with H_2SO_4/NH_4Cl or with $HCl/AlCl_3$ gives an inseparable isomeric mixture of the 1,2-dichloro analog. *cis*- and *trans*-(IIa) undergo stereomutation to form a 1 : 1.9 mixture of these two under the influence of sulfuric acid or ethanol in a hydrocarbon solution. A possible mechanism for this process is discussed in terms of pseudorotation of a pentacovalent, trigonal-bipyramidal silicon intermediate. (Ia) and (IIa) are oxidized stereospecifically to the corresponding cyclic siloxanes in almost quantitative yield by perbenzoic acid, bis(trimethylsilyl) peroxide, and oxygen.

INTRODUCTION

Since 1959[1] a considerable amount of research activity has concentrated around the stereochemistry of reactions on a silicon center, and its achievements greatly owe to Sommer and his coworkers[2] In their studies, almost always optically active α-naphthylphenylmethylsilicon compounds have been used. However, very little attention has been paid to the stereochemistry of compound containing the silicon-silicon bond[3] We have found that *cis* and *trans* isomers of cyclic compounds containing the silicon-silicon bond in the ring are the most suitable materials to investigate the stereochemistry of the silicon-silicon system.

Cyclic compounds practically possess the following merits: (a) resolution of *cis* and *trans* isomers is relatively easy; (b) there are many methods to determine the relative configuration, for which six methods have usually been used[4]; (c) it is possible to discuss the stereochemistry of reactions by using both of the epimeric isomers without optical resolution.

This chapter is concerned with first synthesis and identification of *cis* and *trans* isomers of 1,2-disubstituted-1,2-dimethyl-1,2-disilacyclohexanes, a facile stereomutation of *cis* and *trans*-1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane, and the stereospecific oxidation of the silicon-silicon bond with perbenzoic acid, bis(trimethylsilyl) peroxide and oxygen.

RESULTS AND DISCUSSION

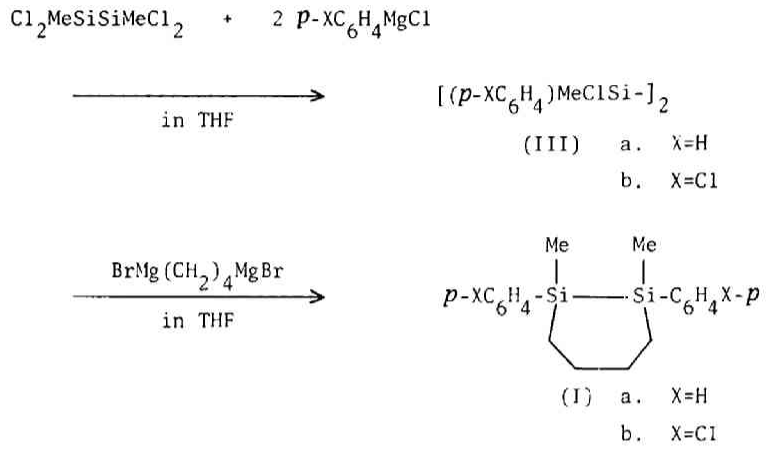
Preparation and Characterization

Some physical properties and analytical data for new compounds (I)-(VII) are summarized in Table 1, and the ^{1}H NMR data, except for (V), in Table 2.

1,2-Diaryl-1,2-dimethyl-1,2-disilacyclohexane

A mixture of *cis*- and *trans*-1,2-diphenyl-1,2-dimethyl-1,2-disilacyclohexane (Ia) was successfully prepared in 75% yield by the reaction of tetramethylenedimagnesium dibromide with 1,2-dichloro-1,2-diphenyl-1,2-dimethyldisilane (IIIa) in tetrahydrofuran (THF). The latter was obtained as a mixture of *meso* and

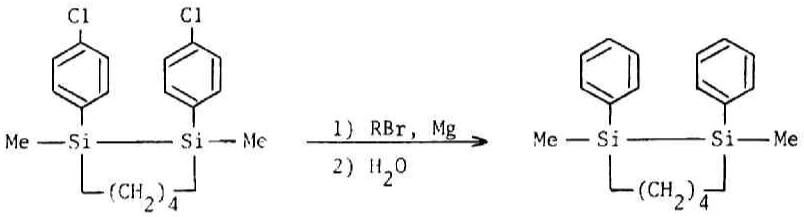
dl compounds in 50% yield through the action of two equivalents of phenylmagnesium chloride on *sym*-tetrachlorodimethyldisilane[5] followed by the crystallization from *n*-hexane.



Either of the isomers of compound (Ia) could be separated pure by several repeated fractional distillations through a spinning band column and/or by preparative GLC. The configurational assignment for the isomeric (Ia) is necessary before any conclusions can be drawn regarding the stereochemistry on silicon atoms. In general, dipole moment measurements provide a very convenient means to characterize geometric isomers of cyclic compounds. In aid of measurements, the cyclic compounds involving some electronegative groups are desired. Accordingly, a mixture of *cis* and *trans* isomers of the *p*-chlorophenyl derivative (Ib) was analogously prepared (70% yield) from the corresponding dichlorodisilane (IIIb). Each of *cis* and *trans* isomers of (Ib) could be isolated by fractional distillation and recrystallization from ethanol. One isomer having a shorter retention time on GLC melts at 43° and another is an oily liquid.

The geometrical configuration of the *p*-chlorophenyl compound (Ib) was established on the basis of the dipole moment data, which were evaluated from measurements of dielectric constants and densities of benzene solutions of each isomer at 25° and from their molar refractions. Thus, one isomer having a shorter retention time on GLC had a higher value, 3.0_2 D, than the other, 2.2_3 D, the results indicating that the former is *cis* and the latter is *trans*.

The assignment of the phenyl derivative (Ia) to *cis*- and *trans*-configuration could be achieved by correlation with the known configuration of the *p*-chlorophenyl derivative (Ib) after Summerbell and co-workers' techniques[6] Thus the action of ethyl bromide and magnesium on both the *cis* and *trans* isomer of the *p*-chlorophenyl derivative (Ib) in tetrahydrofuran, followed by hydrolysis, converted them, with the asymmetric silicon centers intact, into the *cis* and *trans* isomer, respectively, of the phenyl derivative in an excellent yield.



(Ib) *cis* (or *trans*) (Ia) *cis* (or *trans*)

In the early stages of the above investigation, we attempted to obtain compound (I) from the reaction of *sym*-tetraethoxydimethyldisilane[7] with 1 equivalent of a di-Grignard reagent from 1,4-dibromobutane. However, the reaction resulted in the formation of 1-diethoxymethylsilyl-1-methyl-1-silacyclopentane (IV) containing a five-membered ring but no six-membered ring compound was obtained at all. The action of a phenyl Grignard reagent on the fluoro derivative (V), derived from the ethoxy compound (IV) by dissolving it in cold sulfuric acid and then treating with ammonium hydrogen

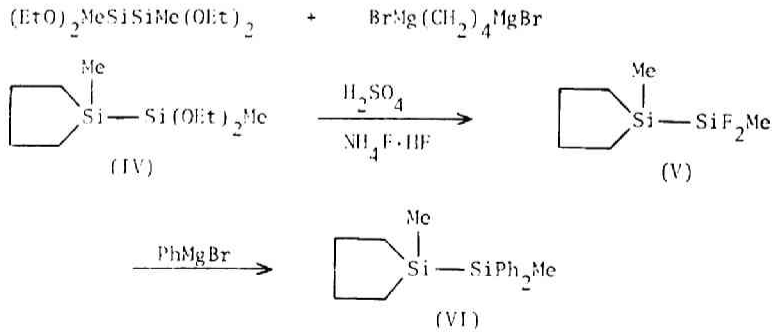


TABLE 1
Physical Constants and Analytical Data for New Compounds (I) – (VII)

Compound	B.p., °C/mm (M.p., °C)	n_D^{20}	d_4^{20}	MR_D Found (Calcd.)	C (%) Found (Calcd.)	H (%) Found (Calcd.)
$C_{18}H_{24}Si_2$ (Ia)						
cis	158/3	1.5847	1.0127	98.11 (98.73)	73.11 (72.90)	8.41 (8.16)
trans	158/3	1.5888	1.0169	98.26 (98.73)	72.71 (72.90)	8.01 (8.16)
$C_{18}H_{22}Cl_2Si_2$ (Ib)						
cis	(43.0-43.5)	---	---	---	59.52 (59.16)	6.17 (6.07)
trans	202-206/2	1.6002	1.1511	108.64 (108.41)	59.39 (59.16)	6.16 (6.07)
$C_6H_{14}F_2Si_2$ (IIa)						
cis	*a*	1.4390	1.0282	46.14 (46.51)	39.96 (39.96)	7.95 (7.82)[b]
trans	*a*	1.4410	1.0331	46.10 (46.51)	39.90 (39.96)	8.00 (7.82)[c]
$C_6H_{14}Cl_2Si_2$ (IIb)[d]	90/18	1.4991	1.0931	57.30 (57.54)	34.24 (33.78)	6.76 (6.62)[e]
$C_{14}H_{16}Cl_2Si_2$ (IIIa)	141-145/2 (67.5-71.0)[g]	---	---	---	54.44 (54.00)	5.24 (5.18)[f]
$C_{14}H_{14}Cl_4Si_2$ (IIIb)	179-183/1.5 (85.0-89.5)[g]	---	---	---	44.61 (44.22)	3.90 (3.71)[h]
$C_{10}H_{24}O_2Si_2$ (IV)	117-118/38	1.4534	0.9078	69.27 (69.35)	51.73 (51.66)	10.53 (10.41)
$C_6H_{14}F_2Si_2$ (V)	147-148	1.4282	1.0013	46.36 (46.72)	*i*	
$C_{18}H_{24}Si_2$ (VI)	161/4	1.5820	1.0030	98.68 (98.73)	73.14 (72.90)	8.13 (8.16)
$C_{18}H_{24}OSi_2$ (VIIa)						
cis	*ca.* 158-160/3	1.5473	---	---	69.74 (69.17)	7.80 (7.74)
trans	*ca.* 160-164/3	1.5479	---	---	69.38 (69.17)	7.71 (7.74)
$C_6H_{14}F_2OSi_2$ (VIIb)						
cis	-----	1.4035	---	---	*j*	
trans	-----	1.4020	---	---	*k*	

[a] B.p. of a mixture of the *cis* and *trans* isomer, 90-95° /100 mm. [b] F%: 20.98 (21.07). [c] F%: 21.27 (21.07). [d] Obtained from the H_2SO_4/NH_4Cl method (see Experimental). [e] Cl%: 33.77 (33.25). [f] Cl%: 22.71 (22.78). [g] The m.p. reported here is the highest value obtained, since it varies with each crop of crystallization. [h] Hydrolyzable Cl%: 18.30 (18.65). [i] F%: 21.42 (21.07). [j] F%: 19.58 (19.35). [k] F%: 19.47 (19.35).

fluoride, yielded 1-diphenylmethylsilyl-1-methyl-1-silacyclopentane (VI). GLC analysis of (VI) showed a homogeneous peak different from the peaks corresponding to the *cis* and *trans* isomers of (Ia). The IR spectra of compounds (IV) and (VI) showed a group of absorption bands characteristic

TABLE 2

^{1}H NMR Data for Compounds (I)–(IV), (VI) and (VII), (τ values)[a]

Compound		CH_3	CH_2	Aromatic
Ia	*cis*	9.61	7.9-9.3	2.4-3.1
	trans	9.68	7.6-9.2	2.3-3.0
Ib	*cis*	9.61	8.1-9.1	2.89
	trans	9.67	7.8-9.2	2.83
IIa	*cis*	9.62[b]	7.8-9.6	----
	trans	9.57[c]	7.8-9.5	----
IIb	*d*	9.43	7.8-9.4	----
IIIa		9.17[e] 9.26	----	2.2-3.1
IIIb		9.14[e] 9.25	----	2.3-2.8
IV[f]		9.86[g]	9.1-9.8[h] 8.2-8.6[i]	----
VI		9.83[j] 9.40[k]	8.1-9.4	2.45-2.9
VIIa	*cis*	9.49	7.95-9.25	2.15-2.75
	trans	9.53	7.85-9.20	2.20-2.80
VIIb	*cis*	9.80[l]	8.85-9.60[h] 8.05-8.55[i]	----
	trans	9.76[l]	7.8-9.7	----

[a] Determined by a JEOL Model C-60H spectrometer in carbon tetrachloride solution. [b] Center of a doublet with $J(^{19}F\text{-}\underline{C}H_3)$ 7.2 cps. [c] Center of a doublet with $J(^{19}F\text{-}\underline{C}H_3)$ 8.4 cps. [d] Possibly a mixture of the *cis* and *trans* isomers. [e] Doublet due to *meso* and *dl* compounds. [f] 8.81 (t., $\underline{C}H_3CH_2O$), 4.28 (q., $CH_3\underline{C}H_2O$). [g] Methyl protons occur as a singlet but at sweep width of 100 cps a doublet results. [h] α to silicon. [i] β to silicon. [j] $Si(\underline{C}H_3)(CH_2)_4$. [k] $Si(\underline{C}H_3)Ph_2$. [l] Center of a doublet with $J(^{19}F\text{-}\underline{C}H_3)$ 6.0 cps.

of the silacyclopentyl group, reported by Nametkin *et al.*[8]

For both cyclic systems (I), the *cis* isomers have lower physical constants (see Table 1) and shorter retention times on GLC (Apiezon-L and

SE 301) than do the *trans* isomers. The proton NMR spectroscopy (see Table 2) showed that the methyl protons in *cis* isomers of both the phenyl and *p*-chlorophenyl derivatives absorb at about 0.07 ppm lower field than those in the *trans* isomers. This is consistent with the above assignments because a somewhat larger effect of magnetic anisotropy of the benzene ring can be expected for the *trans* isomers from inspection of molecular models.

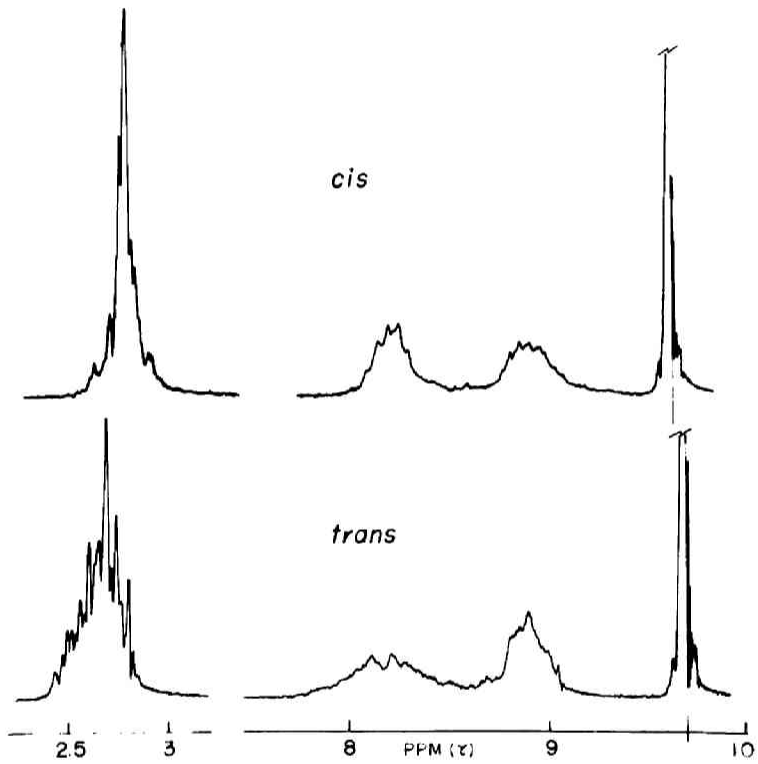


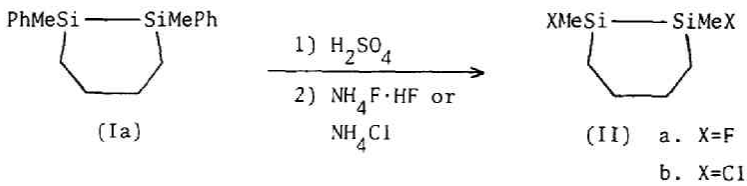
Fig. 1 ^{1}H NMR spectra of *cis*- and *trans*-1,2-diphenyl-1,2-dimethyl-1,2-disilacyclohexane (Ia) in carbon tetrachloride at room temperature (60 Mc).

The spectrum of *cis*-(Ia) shows two groups of multiplets due to the ring methylene hydrogens, while those in the *trans*-(Ia) occur in a more complex, but rather characteristic pattern (Fig. 1). The small differences in the chemical

shifts of the methyl-protons observed in both the dichlorodisilanes (IIIa) and (IIIb) possibly originate from *meso* and *dl* compounds. The similar observations have been reported for a number of *meso* and *dl* compounds[9, 10] Attempts to resolve *meso* and *dl* compounds of (IIIa) by fractional crystallization from *n*-hexane were unrewarding.

1,2-Dihalo-1,2-dimethyl-1,2-disilacyclohexane

When the phenyl derivative (Ia) was fluorodephenylated by dissolving it in concentrated sulfuric acid in the cold and then treating the resulting solution with ammonium hydrogen fluoride, always a mixture of *cis* and *trans* isomers of 1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane (IIa) in a molar ratio of about 1 : 1.9 was obtained regardless of whether the pure *cis* or *trans* isomer of (Ia) or a mixture of both was employed (Table 3).
The total yields were almost quantitative.



(Ia) (II) a. X=F b. X=Cl

TABLE 3

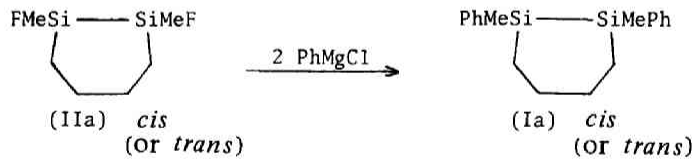
Fluorodephenylation of (Ia)

Isomer ratio in starting (Ia) *cis* : *trans*	Isomer ratio in produced (IIa) *cis* : *trans*
1 : 0	1 : 1.7
0 : 1	1 : 1.9
1 : 1.7	1 : 1.8
1 : 2.1	1 : 1.9
1 4.7	1 : 1.95

This reaction is in contrast with the exclusive cleavage of the silicon-silicon bond observed in the action of sulfuric acid on 1,1,2,2-tetramethyl-1,2-disilacyclohaxane[11](Chapter 1). The result demonstrates that dephenylation of compound (Ia) by sulfuric acid takes place in preference to the cleavage of a slightly strained silicon-silicon bond involved in the 1,2-disilacyclohexane. Furthermore, the silicon-silicon bond linked to some electronegative group(s), in the present case probably hydrogen sulfate group, seems to be reluctant to further attack by sulfuric acid.

These isomers could be separated by preparative GLC. The Silicon DC 550 was the most suitable column packing for the separation of the isomers. The greatest care had to be taken to prevent air oxidation by use of a collecting tube filled with nitrogen, since the fluoro derivative (IIa) was readily oxidized with oxygen even at room temperature. Therefore, measurements of their physical constants and all reactions using them had to be carried out within a day of their purification.

The geometrical identification could be achieved by converting them back into the phenyl derivative (Ia), whose geometrical configuration had been established. Thus, one isomer of (IIa) having a shorter retention time on GLC exclusively gave rise to the *trans*-(Ia), while the other having a longer retention time resulted in predominant formation of the *cis*-(Ia), in excellent yields, upon treatment with phenylmagnesium chloride in tetrahydrofuran.



(IIa) *cis* (or *trans*) (Ia) *cis* (or *trans*)

Since the overall results of this phenylation involved no stereomutation, unambiguous correlation of configuration between (Ia) and (IIa) was thus achieved[4] A small amount of *trans* isomer of (Ia) was produced from *cis*-(IIa), possibly due to the isomerization of the latter *(vide infra)*.

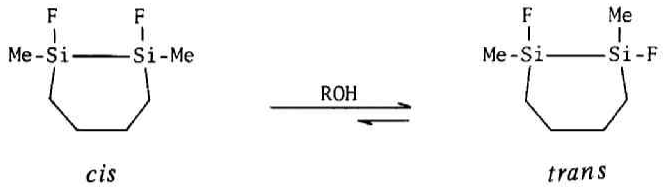
Similarly, but with use of ammonium chloride in place of ammonium hydrogen fluoride, 1,2-dichloro-1,2-dimethyl-1,2-disilacyclohexane (IIb) was

obtained in excellent yield. Compound (IIb) was also obtained by passing dry hydrogen chloride through a solution of (Ia) in chloroform in the presence of aluminum chloride. Upon GLC analysis, compound (IIb) through both methods occurred in a single peak on DC550, Apiezon-L or SE-30 packings. The ^{1}H NMR spectra showed, in addition to multiplets owing to the ring methylene hydrogens, a singlet at τ 9.43 due to the methyl protons. These results were independent of whether one isomer or an isomeric mixture of (Ia) was employed. Upon phenylation with a phenyl Grignard reagent, compound (IIb) was converted back into an isomeric mixture of (Ia). Thus, (IIb) from the former method gave *cis*- and *trans*-(Ia) in the ratio of *ca.* 1 : 2.4 while (IIb) from the latter gave them in *ca.* 1 : 3. If it is reasonably assumed that the reaction of the chloro derivative (IIb) with a phenyl Grignard reagent proceeds in a stereospecific fashion, the isomer ratios of (Ia) formed from (IIb) described above will reflect the isomer ratios of the chloro derivative. It follows that the chlorodephenylation of (Ia) in both the methods presumably occurs nonstereospecifically.

Stereomutation of (IIa)

The fact that the isomeric mixture of (IIa) was obtained from (Ia) would suggest that a process of equilibrium by epimerization may be involved somewhere along the course of the reaction. In addition to the observation in its preparation, however, it was found that the fluoro derivative (IIa) did slowly undergo isomerization during the storage in a sealed tube to afford an isomeric mixture; for example, after 18 days' preservation of the *trans* isomer in a glass ampoule, an isomeric mixture in the ratio of *cis* : *trans*$\simeq$1 : 3.4 was formed. This observation suggests the possibility of stereomutation caused by the action of atmospheric moisture. Indeed, as expected from the observation in its preparation, the fluoro derivative (IIa) in benzene solution did undergo stereomutation very easily when shaken with concentrated sulfuric acid at room temperature to give an isomeric mixture in approximately the same molar ratio as described above. Furthermore, the very facile stereomutation of (IIa) could also be effected by adding a small amount of ethanol to its solution in *n*-hexane or benzene at room temperature. Here

again, an equilibrium mixture of the *cis* and *trans* isomer in the ratio of about 1 : 1.9 was formed.



cis *trans*

Attempts to determine by GLC the rate constants of the ethanol-catalyzed stereomutation of (IIa) were unsuccessful because a few per cent of the fluoro derivative was consumed during the reaction, probably owing to ethanolysis[12,13] Only the apparent *cis* to *trans* equilibrium ratio was obtained (see Fig. 2).

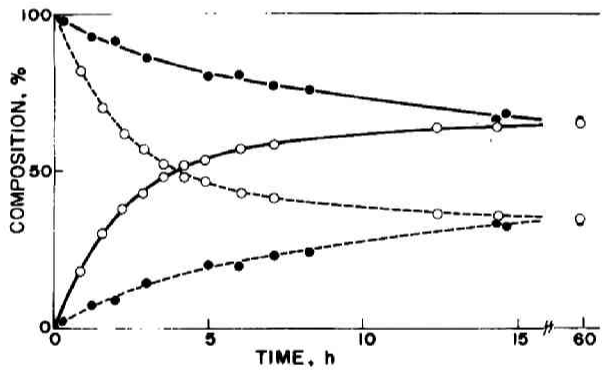
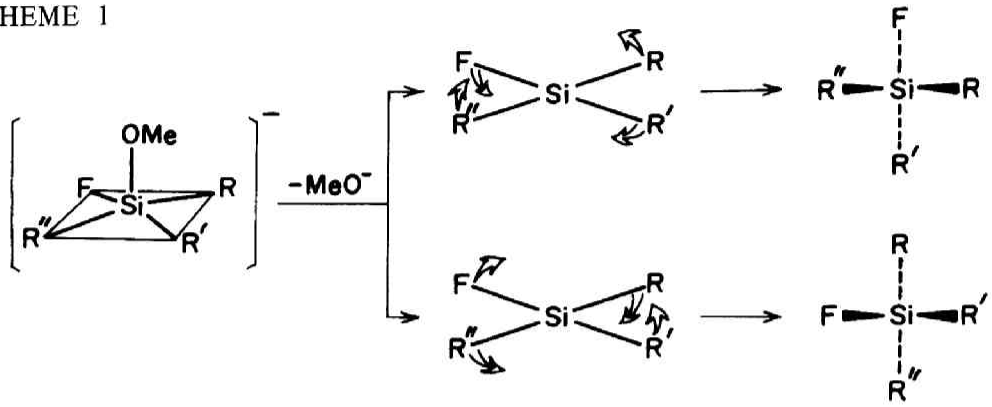


Fig. 2 Equilibration of *cis*- and *trans*-1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane (IIa) by EtOH in benzene solution at 30.0° Concentrations : IIa, 0.15 M; EtOH, 1.00 M. ———, *trans* ; – – – – , *cis*. ○, from *cis;* ●, from *trans*.

The isomerization of the fluoro compound seems similar to racemization of optically active α-naphthylphenylmethylfluorosilane (R_3Si^*F) by the action of methanol in a nonpolar solvent by Sommer *et al.*[14], who proposed a mechanism involving equilibrium formation of a pentacovalent-silicon intermediate, with the organic groups and the fluorine being basal in a tetragonal pyramid, and methoxide being apical. Such an intermediate could return to R_3Si^*F

with retention or inversion of configuration, depending upon which pair of *trans* groups (R and R" or R' and F) move toward the methoxy group as it leaves (see Scheme 1).*

SCHEME 1

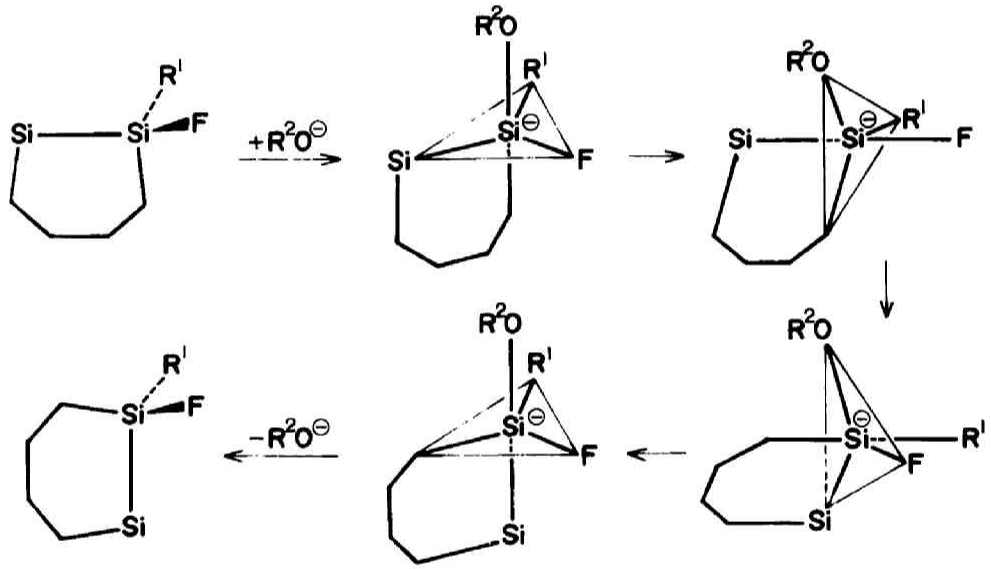


The isomerization of *cis* and *trans* isomer of (IIa) might also proceed *via* a similar intermediate. However, in the present case, the compound under consideration is cyclic. Therefore a more attractive mechanism seems to involve pseudorotation[16] between trigonal-bipyramidal silicon intermediates (Scheme 2). Pseudorotation for compounds of pentacovalent elements has recently been successfully employed for interpretation of isomerization or racemization of various organophosphorus compounds[17] Examination of models reveals that if all skeletal atoms are tetrahedral, namely in sp^3 hybridization, our six membered ring is found to be slightly strained. However, if at least one of the internal bond angles Si-Si-CH_2 deviates from the tetrahedral angle to 90°, the angle strain appears to be reduced. Consequently, if one assumes that a pentacoordinate silicon linked to the alkoxy group is involved in the stereomutation of (IIa), the concept of I-strain may recommend a trigonal-bipyramidal structure rather than a tetragonal-pyramid for structure of the intermediate, since in the trigonal-bipyramidal configuration where the ring occupies one apical and one equatorial position

* In their recent report, Sommer *et al.* have discussed a mechanism involving the pseudorotation process for this racemization[15]

the Si-Si-CH_2 angle can become 90°, whilst in a tetragonal-pyramid where the ring spans two basal positions that angle may be smaller than 90° and when the ring spans one apical and one basal position it may become about 105° (ref. 2). Moreover, it has been shown by theoretical calculations that, in general, the trigonal-bipyramidal configuration is, though slightly, more probable than the tetragonal-pyramid[18,19] In fact, almost all compounds of which structures have been determined by X-ray diffraction possess the trigonal or near trigonal-bipyramidal arrangement[20]

SCHEME 2



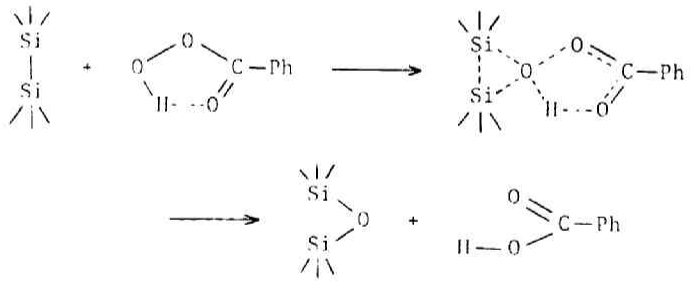
The Scheme 2 illustrates the epimerization of the cyclic compound (IIa) involving pseudorotation. Three times repeated operations of the process followed by leaving of the alkoxy group from the apical position lead to the opposite configuration to that of the starting material, resulting in the stereomutation owing to inversion of one of two asymmetric silicons. Therein, the entering of the alkoxy group as well as leaving may take place at the apical position[17], and the ring spans one apical and one equatorial position all the time to keep the Si-Si-CH_2 bond angle 90° Although more electronegative groups are known to tend to occupy apical positions in at least phosphorus compounds[17, 20a], we believe that in the present case the steric

requirements, *i.e.* the angular requirements described above, exceed the generalization. In fact, recent X-ray structural determinations for pentacoordinate silicon compounds, such as $PhSi(OCH_2CH_2)_3N$[21] and $RSi(o\text{-}O_2C_6H_4)_2$[22], show that they have a slightly distorted trigonal-bipyramidal structure with electronegative groups (oxygen atoms) at the equatorial positions owing to steric constraints.

It has recently been reported that pseudorotation is observed by NMR for SiF_5 and $RSiF_4$ but not for Ph_2SiF_3, and that $R_3SiF_2^-$ can not exist as a ground state species owing to its instability[23] Furthermore, as pointed out by Sommer and Bauman[15], a rapid stereomutation of alkoxysilanes formed from alcoholysis of fluorosilane suggests the possibility of mechanisms other than the pseudorotation route. From these considerations, it should be recognized that the exact mechanism of stereomutation of (IIa) remains rather obscure.

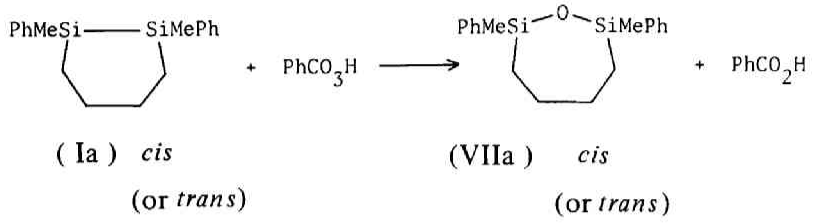
Stereospecific Oxidation of (Ia) and (IIa)

Kumada and his coworkers reported that the silicon-silicon bond is oxidized with perbenzoic acid to form quantitatively the corresponding siloxane bond and, on the basis of kinetic data, a molecular mechanism involving electrophilic attack of the oxygen atom was proposed as follows[24]:



We have now found that the oxidation proceeds in a stereospecific fashion. Thus, both the *cis* and *trans* isomer of the phenyl derivative (Ia) reacted with perbenzoic acid in dichloromethane at room temperature to afford quantitatively *cis*- and *trans*-2,7-dimethyl-2,7-diphenyl-1-oxa-2,7-disilacycloheptane

(VIIa), respectively. Since both the starting isomers gave the different products, it is obvious that no equilibration is involved during the reaction[4]



(Ia) *cis* (or *trans*)　　(VIIa) *cis* (or *trans*)

Consequently, it follows that the isomer of (VIIa) formed from *cis*-(Ia) must be *cis* and the other *trans*. This very high stereospecificity of reaction supports the above molecular mechanism.

As briefly mentioned earlier, the fluoro derivative (IIa) is air-sensitive. When oxygen was passed through the neat liquid at room temperature, both the *cis*- and the *trans*-(IIa) absorbed the gas to give *cis*- and *trans*-2,7-dimethyl-2,7-difluoro-1-oxa-2,7-disilacycloheptane (VIIb), respectively, in about 50% yield, leaving nonvolatile residue. For the initial several hours the reaction proceeded exothermally and, after about fifty hours, about 0.8 equivalent of oxygen was absorbed. The results indicate the stereospecific insertion of oxygen into the silicon-silicon bond. The facile aerobic oxidation of (IIa) is in good contrast with the behavior of compound (Ia) and 1,1,2,2-tetramethyl-1,2-disilacyclohexane (Chapter 1) which are little affected by oxygen, and suggests the acceleration effects by fluorine substitutions.

In connection with the aerobic oxidation, we have investigated the reaction of (Ia) and (IIa) with bis(trimethylsilyl) peroxide (BSPO)[25], and found that the reactions also proceed in the stereospecific fashion to yield the corresponding cyclic siloxane, while BSPO is converted to hexamethyldisiloxane:

Here again, the fluorine derivative (IIa) is much more reactive than the phenyl derivative (Ia), as shown in Table 4.

TABLE 4

Oxidation of (Ia) and (IIa) with BSPO[a]

Compound, mmole	BSPO mmole	Conditions	Product, Yield (%)
RMeSi——SiMeR, $(CH_2)_4$			RMeSi—O—SiMeR, $(CH_2)_4$
(Ia), R Ph			(VIIa), R = Ph
cis 0.354	0.846	80°, 55 h	*cis* 97.7
trans 0.446	0.947	80°, 55 h	*trans* 91.9[b]
(IIa), R F			(VIIb), R F
cis 0.355	0.537	r.t., 1.5 h	*cis* 96.0
trans 0.238	0.356	r.t., 1.5 h	*trans* 96.3

[a] Bis(trimethylsilyl) peroxide. [b] Conversion, *ca.* 92%.

EXPERIMENTAL

cis- and trans-1,2-Diphenyl-1,2-dimethyl-1,2-disilacyclohexane (Ia)

To a di-Grignard reagent from 1,4-dibromobutane, prepared from 6 g (0.25 g-atom) of magnesium and 32 g (0.14 mole) of 1,4-dibromobutane in 250 ml of THF, a solution of 32 g (0.10 mole) of compound (IIIa) in 50 ml of THF was added with cooling in an ice bath over a period of 10 min. After 5-h reflux and removal of solvent by distillation, the remaining mass was hydrolyzed with saturated aqueous solution of ammonium chloride. The organic layer and the extracts were washed with water, sodium bicarbonate and then water, and dried over potassium carbonate. Distillation under reduced pressure gave 25 g of a liquid boiling over the range of 45°-148°/2 mm, along with 6 g of residue. Fractionation through a column packed with glass helices yielded 20 g (74% yield) of (Ia) boiling at 157-159°/4 mm as a mixture of *cis* and *trans* isomer (*cis* : *trans* $\simeq$ 1 : 1.54), n_D^{20} 1.5848. Each isomer was isolated by repeated fractional distillation through a spinning band column. Purification was also possible by preparative GLC (Apiezon-L, 280°).

cis- and trans-1,2-Di-p-chlorophenyl-1,2-dimethyl-1,2-disilacyclohexane (Ib)

Compound (IIIb) (38.0 g, 0.10 mole) diluted with 50 ml of THF was allowed to react with a di-Grignard reagent prepared from 32.6 g (0.15 mole) of 1,4-dibromobutane and 6.8 g (0.28 g-atom) of magnesium in 150 ml of THF. The reaction mixture was worked up in the same manner as described above. Simple distillation gave 34 g of a distillate boiling over the range of 60-205°/1.5 mm, in which the ratio of *cis* to *trans* lay in about unity. Fractional distillation through a short column packed with glass helices afforded the following two fractions: (1) 19 g, b.p. 196-201°/2 mm, consisting of *ca.* 60% of *cis* and 40% of *trans*, and (2) 7.5 g, b.p. 201°/2 mm, *trans*>90%. Total yield of (Ib) was 72%. The *trans* isomer was readily isolated by fractional distillation through a spinning band column, whilst several repeated fractionations and recrystallization from ethanol were required for the purification of the *cis* isomer.

1,2-Dichloro-1,2-diphenyl-1,2-dimethyldisilane (IIIa)

To a solution of 228 g (1.0 mole) of *sym*-tetrachlorodimethyldisilane[5] in 200 ml of THF was added a phenyl Grignard solution, prepared from 51.0 g (2.1 g-atom) of magnesium and 270 g (2.4 mole) of chlorobenzene in 800 ml of THF, over a 2 h-period. The mixture was then refluxed for 10 h. After removal of THF by distillation, the remaining solid was filtered by using 600 ml of ether. The organic layer was distilled to give 272 g of a liquid boiling over the range of 110-200°/3 mm, along with 20 g of residue. Fractionation through a column packed with glass helices gave 161 g (52% yield) of a crystallizable material boiling at 141-146°/2 mm, m.p. 65.0-68.5° (in a sealed tube), which was contaminated with a small amount of 1,1-dichloro-2,2-diphenyl-1,2-dimethyldisilane. The above fraction was, however, used for the preparation of the compound (Ia) without recrystallization. A pure sample of (IIIa) could be obtained by recrystallization from dry *n*-hexane in about 30% yield. The highest melting point of those examined was 67.5-71.0°

1,2-Di-p-chlorophenyl-1,2-dichloro-1,2-dimethyldisilane (IIIb)

The reaction was carried out in essentially the same way as described above, except for use of 294 g (2.0 mole) of *p*-dichlorobenzene instead of chlorobenzene. Distillation gave 230 g of a liquid boiling over the range of 120-225°/3 mm, together with 95 g of residue. Fractional distillation of the above distillate afforded 133 g (36% yield) of a crystallizable material boiling at 170-183°/1.5 mm (mainly 179-183°/1.5 mm). Recrystallization from dry *n*-hexane gave pure (IIIb) in about 19% yield, melting at 85.0-89.5° (in a sealed tube).

Reduction of p-chlorophenyl (Ib) to phenyl derivative (Ia)

From *trans*-(Ib)------ To a mixture of 3.65 g (0.01 mole) of *trans*-(Ib), 6.8 g (0.30 g-atom) of magnesium and 100 ml of THF was added dropwise 31.8 g (0.20 mole) of ethyl bromide in the cold. The mixture was then heated to reflux with stirring for

35 h. A second portion of magnesium (3.4 g, 0.15 g-atom) and ethyl bromide (10.9 g, 0.10 mole) was added to the mixture, which was heated for an additional 16 h. The progress of the reaction was monitored by GLC of a small, extracted and hydrolyzed, sample. The reaction mixture was hydrolyzed and the organic layer and ether extracts were combined, and then distilled to give 3.3 g of an oily liquid boiling over the range of 110-180°/2 mm. Redistillation of this fraction gave 2.5 g (83% yield) of the phenyl derivative (Ia) boiling mainly at 139-141°/1 mm, being almost homogeneous by GLC. The retention time on GLC and NMR spectrum were exactly identical with those of an isomer of (Ia) having a longer retention time. A sample purified by preparative GLC had n_D^{20} 1.5873 (Found: C, 73.10; H, 8.19%).

From *cis*-(Ib) ——— *cis*-(Ib) was treated with ethyl bromide and magnesium in THF in essentially the same manner as described above. The reduced phenyl derivative (Ia) was purified by distillation and by preparative GLC, whose retention time on GLC and NMR spectrum were consonant with those of an isomer of (Ia) having a shorter retention time; n_D^{20} 1.5819 (Found: C, 73.15; H, 8.25%).

Measurement of dipole moment of compound (Ib)[26]

Solvent ——— Benzene was refluxed with anhydrous aluminum chloride (5-10%) for 2 h and distilled, washed to neutral, dried by refluxing over sodium wire and then carefully distilled through a Widmer column.

Apparatus ——— The dielectric constants were measured by the resonance method by using an apparatus built by Dr. K. Kimura, Osaka City University. The circuit diagram had been given by Le Fèvre *et al.*[27] The dielectric constant cell of an Azuma type[28], equipped with three concentric nickel electrodes, had the capacity of about 100 pF and a volume of *ca.* 10 ml. The densities of the solutions were measured in a pycnometer of a modified Lipkin type.

Procedure ——— Three or four solutions of each isomer in benzene were used with weight fractions between 0.002 and 0.02. They were prepared in glass-stoppered Erlenmeyer flask and stored in a desiccator. The measurements were made in a large thermostat maintained at 25.0°, filled with an oil which was stirred well. The dielectric cell was calibrated with air and with pure benzene, and the pycnometer with benzene.

Results ——— The dipole moments were obtained from the Debye equation:

$$\mu = 0.0128\sqrt{(P_2 - 1.05MR_D)T} \qquad (D)$$

The MR_D value was obtained by addition of bond refractions. The value of P_2 is given by the formula

$$P_2 = \frac{\epsilon_1 - 1}{\epsilon_1 + 2}\cdot\frac{M_2}{d_1}\left(1 + \frac{3a}{(\epsilon_1 - 1)(\epsilon_1 + 2)} - \frac{b}{d_1}\right)$$

The coefficients a and b, defined by the equations,

$$\epsilon_{12} = \epsilon_1 \quad a\omega_2$$

$$d_{12} = d_1 \quad b\omega_2$$

were determined from the plot of ϵ_{12} and d_{12} versus ω_2, which are recorded in Tables 5 and 6.

The notations used here are: ϵ_1 and d_1, dielectric constant and density of solvent; ϵ_{12} and d_{12}, those of solution; ω_2, weight fraction of solute; M_2, molecular weight of solute; P_2, molar polarization of solute at infinite dilution.

Reaction of sym-tetraethoxydimethyldisilane with tetramethylenedimagnesium dibromide

To a Grignard reagent, prepared from 22 g (0.92 g-atom) of magnesium and 110 g (0.51 mole) of 1,4-dibromobutane in 500 ml of ether, was added a solution of 100 g (0.38 mole) of *sym*-tetraethoxydimethyldisilane[7] in 200 ml of ether in the cold over a period of 20 min. The reaction mixture was stirred at room temperature for 2 h and then refluxed for 4 h. After removal of about 400 ml of ether, the remainder was heated for an additional 20 h. The resulting mass was filtered by use of about 200 ml of ether and the salt was washed with several 100 ml portions of ether. The filtrate was distilled to give, together with 41 g of residue, 24 g (27% yield) of 1-diethoxymethylsilyl-1-methyl-1-silacyclopentane (IV) as a colorless liquid homogeneous by GLC. The IR spectrum showed a group of bands at 1080, 1027 and 1033 cm^{-1} characteristic of the silacyclopentyl ring[8]

1-Difluoromethylsilyl-1-methyl-1-silacyclopentane (V)

With cooling in an ice bath, to vigorously stirred concentrated sulfuric acid (200 g) was added dropwise 30 g (0.13 mole) of 1-diethoxymethylsilyl-1-methyl-1-silacyclopentane over a period of 30 min. After the addition was completed, 28 g (0.5 mole) of ammonium hydrogen fluoride was added in several portions at the same temperature. The resulting organic layer was flash-distilled under reduced pressure and the subsequent fractional distillation gave 16 g (68% yield) of compound (V)

1-Diphenylmethylsilyl-1-methyl-1-silacyclopentane (VI)

To a phenyl Grignard reagent, prepared from 5 g (0.20 g-atom) of magnesium and 35 g (0.22 mole) of bromobenzene in 50 ml of ether, was added 15 g (0.083 mole) of 1-difluoromethylsilyl-1-methyl-1-silacyclopentane over 10 min, and the mixture was then refluxed for 15 h. Work-up and fractional distillation gave 18 g (55% yield) of 1-diphenylmethylsilyl-1-methyl-1-silacyclopentane (VI). The IR spectrum showed a group of absorption bands at 1080, 1027 and 1035 cm^{-1} characteristic of the silacyclopentyl ring[8]

TABLE 5

Compound (Ib) with a Shorter Retention Time (*cis*)

$\omega_2 \times 100$	ε_{12}	$\omega_2 \times 100$	d_{12}
0	(2.2710)[a]	0	0.87283
0.2343	2.2785	0.3221	0.87352
0.5616	2.2875	1.527	0.87596
1.2088	2.3071	1.909	0.87673
1.8440	2.3258		
a 2.97		b 0.205	
$\mu = 3.0_2$ D			

[a] Intercept.

TABLE 6

Compound (Ib) with a Longer Retention Time (*trans*)

$\omega_2 \times 100$	ε_{12}	$\omega_2 \times 100$	d_{12}
0	(2.2712)[a]	0	0.87283
0.2959	2.2767	0.2485	0.87336
0.6926	2.2832	0.6006	0.87405
1.236	2.2930	1.415	0.87573
1.929	2.3048		
a 1.75		b 0.205	
μ 2.2_3 D			

[a] Intercept.

The product was homogeneous by GLC and had a shorter retention time than both the *cis*- and *trans*-1,2-diphenyl-1,2-dimethyl-1,2-disilacyclohexane (Ia).

cis- and trans-1,2-Dimethyl-1,2-difluoro-1,2-disilacyclohexane (IIa)

In a typical run, to a stirred concentrated sulfuric acid (98 g; 1.0 mole) was added 29.7 g (0.1 mole) of compound (Ia) (*cis* : *trans* ≃ 1 : 1.66) in the cold (below 3°) over a period of 1.5 h and the mixture was then stirred for an additional 2 h at the same temperature. With cooling, 13 g (0.228 mole) of ammonium hydrogen fluoride was then added in several portions. Distillation of an organic layer under a nitrogen stream gave 16.5 g (92% yield) of the fluoro derivative (IIa), as an isomeric mixture in the ratio of *cis* : *trans* ≃ 1 : 1.82, boiling over the range of 90-95°/100 mm. Each isomer was isolated by preparative GLC (Silicon DC 550, 110°). A collecting tube had to be equipped for a nitrogen atmosphere, since the fluoro derivative (IIa) was readily oxidized with oxygen even at room temperature.

Analogously, 1 g of the pure *cis*-(Ia) was treated with 2 g of H_2SO_4 and then with ammonium hydrogen fluoride (1 g) with cooling. An isomeric mixture of (IIa) in the ratio of *cis* : *trans* ≃ 1 : 1.69 was formed. The ratio of *cis* to *trans* isomer of (IIa) formed from the pure *trans*-(Ia) also lay in about 1 : 1.86. These data are collected in Table 3.

Phenylation of (IIa)

From an isomer having the shorter retention time——— An isomer (0.15 g) having the shorter retention time on GLC, freshly isolated, was treated with phenylmagnesium chloride in THF. Predominant formation of *trans* isomer of (Ia), *cis* : *trans* ≃ 3 : 97, was shown by GLC analysis of a hydrolyzed sample of the reaction mixture. The ^1H NMR spectrum of the product isolated by preparative GLC was superimposable with that of the authentic sample of *trans*-(Ia). In another run, essentially the same result was obtained.

From an isomer having the longer retention time——— Similarly, an isomer (0.14 g) of (IIa) having the longer retention time was phenylated, resulting in the predominant formation of *cis* isomer of (Ia), *cis* : *trans* ≃ 91 : 9. The retention time on GLC and the ^1H NMR spectrum of the products were coincident with those of the authentic samples. In another run, essentially the same result was obtained.

1,2-Dichloro-1,2-dimethyl-1,2-disilacyclohexane (IIb)

(a) To cold concentrated sulfuric acid (98 g; 1 mole) was added dropwise 14.8 g (0.05 mole) of (Ia) (*cis* : *trans* ≃ 1 : 1.7) with vigorous stirring over a period of 1.5 h. After an additional 2 h stirring, 16 g (0.3 mole) of ammonium chloride was added in several portions with cooling. Flash distillation and subsequent fractionation of the separated organic layer gave 8.2 g (77% yield) of (IIb) boiling at 90°/18 mm.

(b) To a solution of 15 g (0.051 mole) of *cis*-(Ia) in 100 ml of chloroform was added 0.8 g of freshly sublimed aluminum chloride. Dry hydrogen chloride was passed through the above mixture in the cold (an ice bath) for the first 1 h and then at room temperature for 14 h. Evaporation of chloroform under reduced pressure was followed by fractional distillation through a short column packed with glass helices to afford 5.5 g (51% yield) of (IIb) having b.p. 107-108°/35 mm, n^{20}_D 1.4972, d^{20}_4 1.0904; MR_D 57.25. (Found: C, 34.31; H, 6.90; Cl, 32.70%).

The similar reaction using 21 g (0.071 mole) of *trans*-(Ia), 1 g of aluminum chloride and 150 ml of chloroform yielded 8.5 g (56% yield) of (IIb); b.p. 102°/27 mm, n^{20}_D 1.4973, d^{20}_4 1.0915; MR_D 57.21. (Found: C, 33.76; H, 6.78; Cl, 33.34%).

The NMR spectra of (IIb) obtained from all the above methods revealed that the methyl group protons absorb at 9.43 τ as a singlet. Compound (IIb) was almost homogeneous by GLC on all packing materials examined (Silicon DC550, Apiezon-L and SE30).

Phenylation of (IIb)

By the method (a) described above, the pure *cis*-(Ia) was treated with sulfuric acid (10 g) and subsequently with ammonium chloride (3 g). The organic layer was phenylated with excess phenylmagnesium chloride in THF to form, after hydrolysis, an isomeric mixture of (Ia) in the ratio of *cis* : *trans* $\simeq$ 1 : 2.3. With *trans*-(Ia), the similar result (*cis* : *trans* $\simeq$ 1 : 2.5) was obtained.

Compound (IIb) obtained from *cis*-(Ia) by the method (b) above was treated with excess phenylmagnesium chloride to give a mixture of *cis*- and *trans*-(Ia) in the ratio of about 1 : 2.8. Phenylation of (IIb) from *trans*-(Ia) also resulted in the formation of an isomeric mixture of (Ia) in the ratio of *cis* : *trans* $\simeq$ 1 : 3.2.

Stereomutation of cis- and trans-(IIa)

By the action of H_2SO_4 ——— A pure sample of the *cis* isomer of (IIa) (*ca.* 0.05 g), benzene (1 ml) and concentrated H_2SO_4 (1 ml) were shaken at room temperature. The progress of the isomerization was followed by GLC. The equilibration was already accomplished after about 1 h. Addition of ammonium hydrogen fluoride did not change the isomeric ratio of *cis* : *trans* $\simeq$ 1 : 1.82.

Similarly, the *trans* isomer (0.1 g), benzene (1 ml) and H_2SO_4 (2 g) were combined and shaken at room temperature. Equilibration was achieved after about 3 h. The ratio of *cis* to *trans* lay in about 1 : 1.83.

By the action of EtOH ——— The *cis* isomer (35 μl), EtOH (20 μl) and *n*-hexane (1 ml) were combined and allowed to stand at room temperature. The progress of the isomerization was followed by GLC. The relatively slow isomerization was observed. After overnight, the ratio of *cis* to *trans* was about 1 : 2.21.

A solution of the *trans* isomer (30 μl) and EtOH (30 μl) in 1 ml of benzene

was allowed to stand at room temperature. The isomerization was of much slower than that under the influence of H_2SO_4. After 45 h, the ratio of *cis* to *trans* was 1 : 1.99.

The progress of the isomerization of *cis* and *trans* isomers of compound (IIa) under the influence of ethanol in benzene solution was measured. Each isomer was used within a day of purification, because the compound is readily oxidized by air and isomerized to each other even by moisture. All vessels used here (measuring flasks, pipettes and reaction vessels) were filled with nitrogen. The reaction vessel was a glass-stoppered 10-ml test tube. To carry out a rate experiment, a solution of the sample (2.0 ml) was placed in the test tube, which was immersed in a thermostat bath (30.0 ± 0.1°), and the solution of ethanol (2.0 ml) was then added rapidly. The decrease in amounts of one isomer and the increase of another were analyzed at intervals through the course of the reaction by GLC (Silicon DC550, 89°, He flow rate 12-13 ml/min). The results are ploted against time in Fig. 2.

Reaction of (Ia) with Perbenzoic Acid

To compound (Ia) (1.5 g; 5 mmole) was added a solution of perbenzoic acid (13.5 mmole) in methylene chloride (25 ml) and the mixture was allowed to stand overnight at room temperature. GLC analysis showed that the starting material was completely consumed, while a new homogeneous product formed quantitatively. After washed with saturated aqueous solution of sodium bicarbonate to remove benzoic acid formed and excess of the peracid, the product was isolated by preparative GLC. *cis*-(Ia) formed the *cis* isomer of the corresponding cyclic disiloxane, 2,7-diphenyl-2,7-dimethyl-1-oxa-2,7-disilacycloheptane (VIIa).

Similarly, *trans*-(Ia) yielded *trans*-(VIIa).

The IR spectrum showed the absorption band characteristic of the siloxane bond at 1013 cm^{-1} for both the *cis*- and *trans*-(VIIa). The retention time on GLC of the *cis*-(VIIa) was shorter than that of the *trans* isomer.

Oxidation of (IIa) with Oxygen

Oxygen was passed through 1.8 g (10 mmole) of *cis*-(IIa) at room temperature. Slightly exothermic reaction occurred for the initial several hours. After 59 h, 205 ml of oxygen was absorbed and GLC analysis revealed that the starting material was no longer present. The volatile product was distilled under reduced pressure (boiling up to 55°/15 mm) to give 1.2 g of *cis*-2,7-difluoro-2,7-dimethyl-1-oxa-2,7-disilacycloheptane (VIIb), leaving 0.5 g of residue. The product was almost homogeneous by GLC and the stereospecificity was over 97%. Preparative GLC (Silicon DC550, 135°) afforded a pure sample of the siloxane (VIIb).

trans-(IIa) was allowed to react with oxygen for 40 h in essentially the same manner as described above. Distillation yielded 1.1 g of *trans*-(VIIb), together with 0.5 g of residue. After purification by preparative GLC, the siloxane showed n_D^{20} 1.4020

(Found: F, 19.47%). Th stereospecificity was again over 97%. The IR spectrum showed a strong band at 945 cm^{-1} due to ν(Si-O) for both the *cis*- and *trans*-(VIIb).

Reaction of (Ia) and (IIa) with bis(trimethylsilyl) peroxide

Bis(trimethylsilyl) peroxide was prepared in essentially the same manner reported by Hahn and Metzinger [25], except using 90% hydrogen peroxide in place of anhydrous peroxide. Moreover, to remove hydrogen chloride formed, ammonia was used in place of pyridine.

The reactions were carried out in a small, sealed glass tube. The GLC analysis revealed that the reaction proceeded in a stereospecific fashion to form the corresponding cyclic siloxane, as well as hexamethyldisiloxane arising from the peroxide. The product was isolated by preparative GLC and their IR spectra were compaired with those of authentic samples. The yield was estimated by GLC by comparison of the peak areas with the area of a standard substance added. For the reaction of (Ia) it was necessary to heat for a prolonged period of time, whilst the reaction of (IIa) was slightly exothermic.
The results are collected in Table 4.

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CHAPTER THREE

cis- AND *trans*-9,10-DIMETHYL-9,10-DISILADECALIN. SYNTHESIS AND OXIDATION WITH PEROXIDES

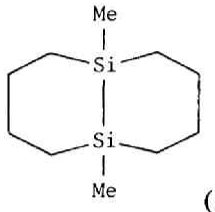
SUMMARY

The reaction of the *cis* isomer of 1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane (IIb) with $BrMg(CH_2)_4MgBr$ gave the *cis* isomer of 9,10-dimethyl-9,10-disiladecalin (I) as the sole product. On the other hand, the reaction with the *trans* isomer of (IIb) yielded a mixture of *cis* and *trans* isomers of (I) in the ratio of 1 : 0.6. The structure assignment of (I) was based mainly on the NMR spectra. Both the *cis* and *trans* isomers of (I) underwent oxidation very easily when treated with perbenzoic acid, giving the *cis* isomer of 1,6-dimethyl-11-oxa-1,6-disilabicyclo[4.4.1]undecane (IV). No *trans*-(IV) was formed at all. Oxidations with bis(trimethylsilyl) peroxide and oxygen afforded the similar results. A mechanism for the formation of *cis*-(IV) from *trans*-(I) in the perbenzoic acid oxidation is proposed.

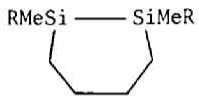
INTRODUCTION

In the preceding chapter, we described the preparation and stereochemistry of geometric isomers of 1,2-disubstituted-1,2-dimethyl-1,2-disilacyclohexane (II). Therein, it was mentioned that the silicon-silicon bond involved in the 1,2-disilacyclohexane ring is slightly strained. The construction of molecular models reveals that in the fused ring system such as 9,10-disiladecalin the *trans* isomer is more strained than the *cis* isomer. It is therefore expected that the difference might be reflected in the formation and the reaction of such compounds.

This chapter concerns the stereochemistry of the formation of *cis*- and *trans*-9,10-dimethyl-9,10-disiladecalin (I) from compounds (IIb) and (IIc), and of the oxidation of (I) with perbenzoic acid, bis(trimethylsilyl) peroxide and oxygen.



(I)

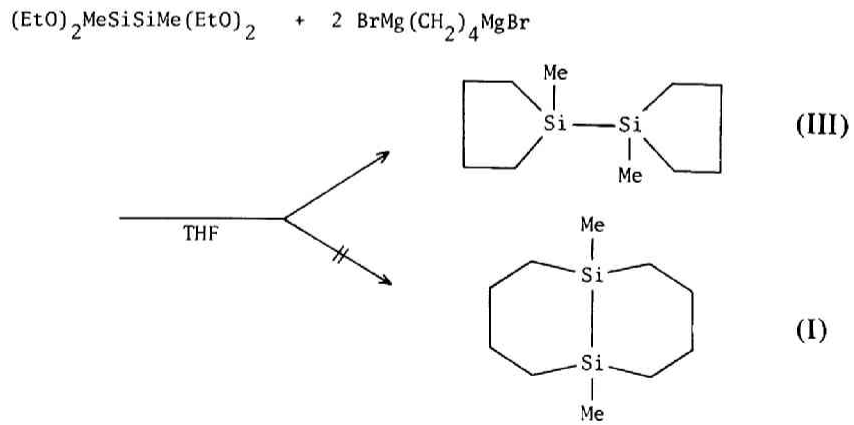


(II) a. R = Ph
b. R = F
c. R = Cl

RESULTS AND DISCUSSION

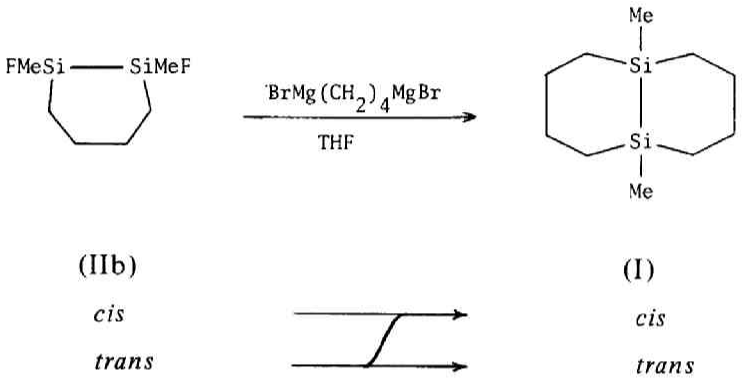
Preparation and Characterization

Attempts to prepare 9,10-dimethyl-9,10-disiladecalin (I) by the action of a di-Grignard reagent from 1,4-dibromobutane on *sym*-tetraethoxydimethyldisilane[1] in tetrahydrofuran (THF) resulted, as described in Chapter 2, in the formation of its structural isomer, bis(1-methyl-1-silacyclopentyl) (III), containing five-membered rings instead of six-membered ones. The IR spectrum of (III) showed a group of bands characteristic of the silacyclopentyl ring reported by Nametkin *et al.*[2]



9,10-Dimethyl-9,10-disiladecalin (I) could be obtained from 1,2-difluoro-

1,2-dimethyl-1,2-disilacyclohexane (IIb) (see Chapter 2) and from the chloro analog (IIc) (see Chapter 2) by treating them with a di-Grignard reagent from 1,4-dibromobutane in THF Thus, the reaction of the *cis* isomer of (IIb) with $BrMg(CH_2)_4MgBr$ gave the *cis* isomer of compound (I) as the sole product, while a mixture of *cis* and *trans* isomers of (I) in the ratio of 1 : 0.6 was produced from *trans*-(IIb). From the chloro derivative (IIc) only the *cis* isomer of (I) was obtained in 56% yield.



Each isomer was isolated by fractional distillation and subsequent preparative GLC. The *trans* isomer of (I) was purified by recrystallization from methanol under a nitrogen atmosphere because of its air-sensitivity.

The structure assignment of (I) is based on the following considerations. As in the conversion of (IIb) into (IIa) described in Chapter 2, the replacement of the two fluorine atoms with a Grignard reagent would proceed stereospecifically, provided that no substantial amount of strain is present in the reaction product. Inspection of molecular models reveals that *trans*-(I) is fairly highly strained whereas the *cis* isomer is not. Therefore the sole product from *cis*-(IIb) should be *cis*. These relationships are in contrast with the fact that the *trans* isomer of decalin is more stable than the *cis*, and are very similar to those observed for *cis* and *trans* isomers of bicyclo[3.3.0]octane.[3]

It is well known that *trans*-decalin is locked, whereas *cis*-decalin has the interconvertible enantiomeric conformers[3,4] Therefore it follows that the ^1H NMR spectra show broad, complex signals for the former, while a sharp singlet for the latter[3, 5, 6] Also in the present case, the ^1H NMR spectra of (I)

show that the *trans* isomer is a rigid molecule, while the *cis* isomer has two interchangeable limiting structures. As shown in Fig. 1, the spectrum of

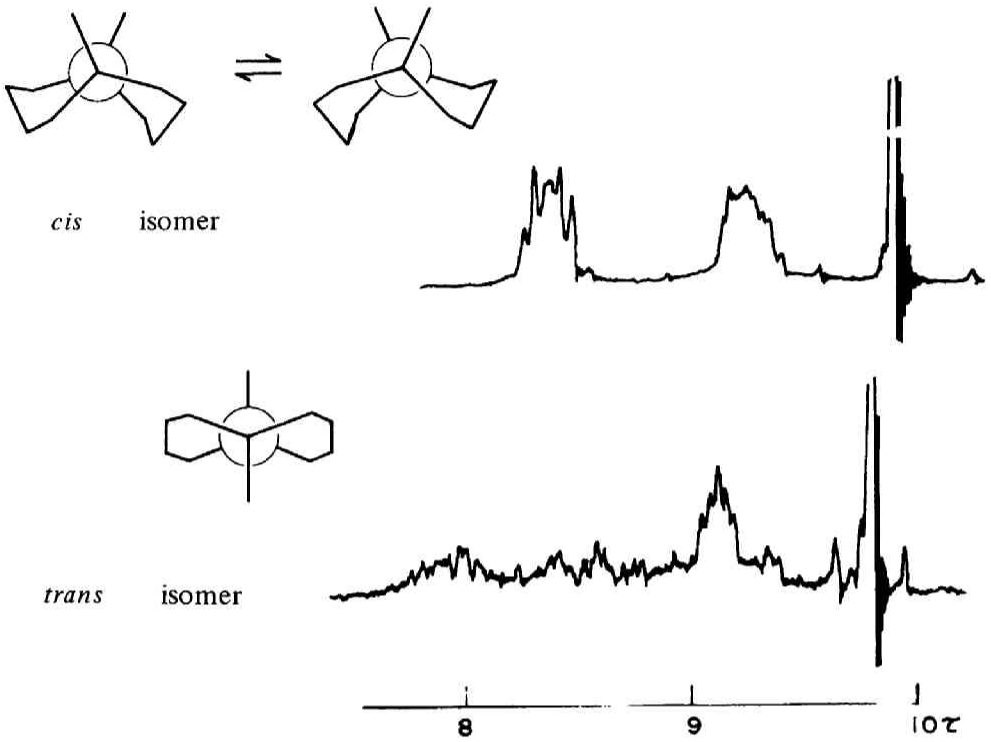


Fig. 1 ^{1}H NMR spectra of *cis*- and *trans*-9,10-dimethyl-9,10-disiladecalin (I) in carbon tetrachloride at room temperature (60 Mc).

cis-(I) shows two groups of multiplet bands due to the ring methylene hydrogens; since, because of the rapid flipping of the molecule from one form to the other, the methylene hydrogens fall into two groups and those of each group are in an average position as far as the NMR spectrum is concerned. The whole pattern of the spectrum is very similar to that for *cis*-(IIa) (see Fig. 1 in Chapter 2), except for the peaks due to the phenyl groups. The *trans* isomer of (I), on the other hand, shows a very complex band caused by the non-equivalent equatorial and axial hydrogens at two

different kinds of positions and complicated by spin-spin coupling. The whole pattern of the spectrum resembles that of *trans*-(IIa) (see Fig. 1 in Chapter 2) more closely than that of *cis*-(IIa).

Physical properties and analytical data for compounds (I) and (III) are listed in Table 1.

TABLE 1

Physical Properties and Analytical Data for Compounds (I), (III) and (IV)

Compound		B.p. (°C/mm) (M.p., °C)	n_D^{20}	d_4^{20}	MR_D	C(%)	H(%)
$C_{10}H_{22}Si_2$	(I)						
cis		109/17	1.5123	0.9158	65.06[a]	60.52[b]	11.01[c]
trans		(93.5-94.5)	---	---	---	60.71[b]	11.26[c]
$C_{10}H_{22}Si_2$	(III)	126-127/37	1.5033	0.8967	65.47[a]	60.35[b]	11.39[c]
$C_{10}H_{22}OSi_2$	(IV)	---	---	---	---	56.86[d]	10.22[e]

[a] Calcd.: 65.32. [b] Calcd.: 60.52. [c] Calcd.: 11.17. [d] Calcd.: 56.00. [e] Calcd.: 10.34.

Oxidation with Peroxides

Kumada and his coworkers[7] reported that the silicon-silicon bond is oxidized with perbenzoic acid to give quantitatively the corresponding siloxane. In the preceding chapter, it has been described that the oxidation of the silicon-silicon bond with perbenzoic acid, and also with bis(trimethylsilyl) peroxide and oxygen, proceeds quite stereospecifically, unless substantial amounts of ring strain and steric hindrance are involved in the product, as observed in the oxidation of compounds (IIa) and (IIb). We have now investigated the oxidation of *cis*- and *trans*-(I) with perbenzoic acid, bis(trimethylsilyl) peroxide[8] and oxygen.

Both the *cis* and *trans* isomers of (I) were found to undergo oxidation very easily when treated with perbenzoic acid at room temperature for 2 h

to give the *cis* isomer alone of 1,6-dimethyl-11-oxa-1,6-disilabicyclo[4.4.1]-undecane (IV). The yield was almost quantitative from *cis*-(I) and 83% from *trans*-(I). The oxidation with bis(trimethylsilyl) peroxide at 80° for 50 h also converted both *cis*- and *trans*-(I) into the *cis*-siloxane (IV), in *ca.* 100 and 22% yield, respectively. In the latter case, considerable amounts of non-volatile polysiloxanes were formed as the byproduct. The *trans*-(I) was slowly oxidized in air and more easily under an oxygen atmosphere to give *cis*-(IV), together with polysiloxanes, whilst the *cis*-(I) was stable even under the influence of oxygen.

The IR spectrum of the product (IV) showed the intense absorption band at 992 cm^{-1} characteristic of the siloxane bond. The assignment to the *cis* form comes from the following reasons. As mentioned in the preceding chapter, the oxidation of a silicon-silicon bond with perbenzoic acid and bis(trimethylsilyl) peroxide proceeds quantitatively and in a stereospecific fashion, if there is no substantial amount of ring strain and steric hindrance in the product. As shown in Fig. 2, inspection of molecular models reveals that the *trans*-siloxane (IV) involves unfavorable, serious constellation effects

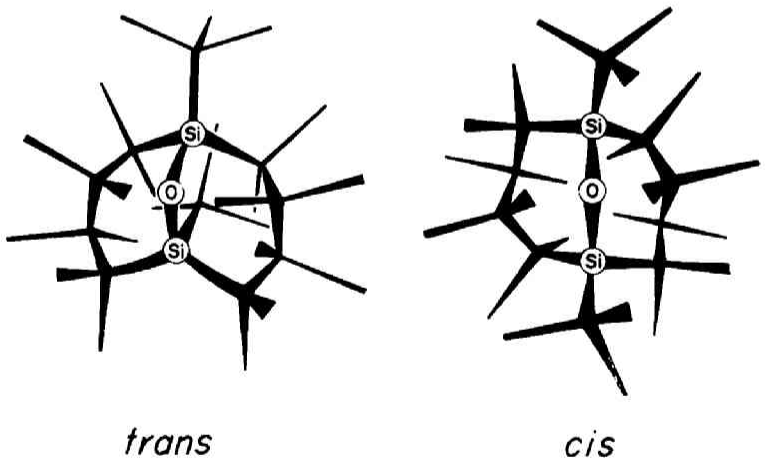
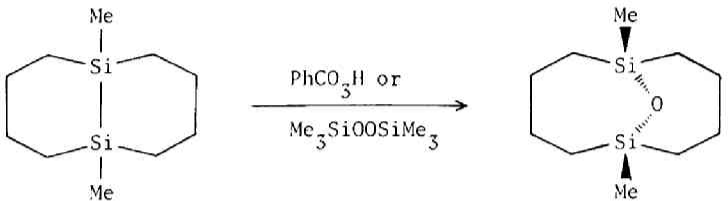
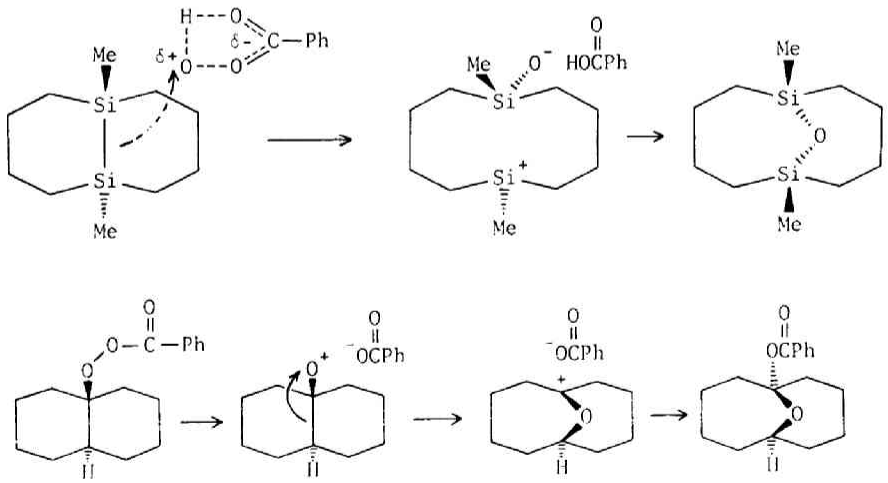


Fig. 2 Framework molecular models of *cis*- and *trans*-1,6-dimethyl-11-oxa-1,6-disilabicyclo[4.4.1]undecane (IV).

whereas the *cis*-siloxane does not. Therefore, the product obtained in quantitative yield from *cis*-(I) should be of the *cis* form, and the oxidation of *trans*-(I) must have taken place with complete stereomutation.



Perbenzoic acid is regarded as an electrophilic reagent for at least aliphatic polysilanes[7] The stereomutation observed in the oxidation of the *trans*-(I) may be rationalized in terms of the inversion of a "siliconium ion" which might arise at the moment of electrophilic attack of the peracid on the silicon-silicon bond. It is interesting to compare this reaction with the rearrangement of *trans*-9-decalyl perbenzoate involving migration of carbon to positive oxygen through an intermediate of "intimate ion-pair" type[9]



EXPERIMENTAL

All reactions were carried out under a nitrogen atmosphere. The reaction using 1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane (IIb) had to be carried out within a day of its purification, for the fluoro derivative underwent *cis-trans* isomerization and was readily oxidized with oxygen (see Chapter 2). Infrared spectra were measured on a Hitachi EPI G3 Grating spectrophotometer. NMR spectra were obtained on a JEOL Model C-6OH spectrometer in carbon tetrachloride solution.

Preparation of cis- and trans-9,10-dimethyl-9,10-disiladecalin (I)

(1) From an isomeric mixture of *cis-* and *trans*-1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane (IIb). A solution of 16 g (0.089 mole) of (IIb), consisting of the *cis* and *trans* isomers (*cis* : *trans* $\simeq$ 1 : 2), in 100 ml of THF was added to a Grignard solution, prepared from 28.8 g (0.133 mole) of 1,4-dibromobutane and 6.6 g (0.27 g-atom) of magnesium in 300 ml of THF, over 1 h at room temperature. The reaction mixture was heated with stirring for 5 h and then about 300 ml of THF was removed by distillation. After an additional 2-h reflux, the reaction mixture was hydrolyzed and worked up in the usual manner. Fractional distillation gave 7.0 g (39.5% yield) of a mixture of *cis-* and *trans*-9,10-dimethyl-9,10-disiladecalin (*cis* : *trans* $\simeq$ 1 : 0.47) boiling over the range of 118.5-127°/21 mm, together with 2 g of forerun and 9.0 g of residue. Each isomer was isolated by preparative GLC (230°, Apiezon-L, Varian Model 90P) and the *trans* isomer was re-crystallized from methanol under nitrogen. Since the *cis* isomer had the same retention time on GLC as the siloxane (IV), it was usually contaminated with a small amount of (IV). Therefore, the *cis* isomer was purified by treatment with cold concentrated sulfuric acid and washing with saturated aqueous solution of sodium bicarbonate and water to neutral, and by redistillation. The identity was established by molecular weight determination by mass spectroscopy (Found: 198; $C_{10}H_{22}Si_2$ calcd.: 198.47), elementary analysis (Table 1) and the NMR spectra (Fig. 1).

(2) From *cis*-(IIb). The *cis* isomer of (IIb) (0.45 g; 2.5 mmole) was treated with the di-Grignard reagent, prepared from 1.6 g (66 mg-atom) of magnesium and 5.9 g (27.5 mmole) of 1,4-dibromobutane in 20 ml of THF. under reflux conditions for 5 h. After work-up in the usual way, the reaction mixture was flash-distilled to give 0.39 g of a viscous oil boiling over the range of 60-130°/12 mm. The presence of the *cis* isomer alone of (I) was revealed by GLC analysis of the distillate.

(3) From *trans*-(IIb). Similarly, the freshly purified *trans* isomer of (IIb) (2.0 g; 11.0 mmole) was allowed to react with tetramethylenedimagnesium dibromide, prepared from 10.8 g (50 mmole) of 1,4-dibromobutane and 3.0 g (123 mg-atom) of magnesium in 60 ml of THF. After work-up of the reaction mixture, distillation gave 2.0 g of a

colorless liquid boiling up to 120°/15 mm. It consisted of an isomeric mixture of *cis*- and *trans*-(I) in the ratio of about 1 : 0.57, together with one other product in nearly equal amount to the *trans* isomer, possibly 1,2-dibutyl-1,2-dimethyl-1,2-disilacyclohexane (Found: C, 65.40; H, 12.62. $C_{14}H_{32}Si_2$ calcd.: C, 65.53; H, 12.57%).

(4) From 1,2-dichloro-1,2-dimethyl-1,2-disilacyclohexane (IIc). To a Grignard solution, prepared from 22.7 g (0.11 mole) of 1,4-dibromobutane and 5.6 g (0.23 g-atom) of magnesium in 100 ml of THF, was added a solution of 14.9 g (0.07 mole) of (IIc) in 100 ml of THF at room temperature with stirring over 40 min. After the addition was completed, the reaction mixture was stirred at room temperature for 1 h and then refluxed for 6 h. About 150 ml of THF was removed by distillation. Hydrolysis of the remaining mass with dilute acid and distillation of the organic layer under reduced pressure gave 8.5 g of a liquid boiling over the range of 103-113°/20 mm, along with 4.5 g of residue. Fractionation afforded 7.8 g (56% yield) of *cis*-(I) homogeneous by GLC.

Bis(1-methyl-1-silacyclopentyl) (III)

To a di-Grignard solution, prepared from 24 g (1 g-atom) of magnesium and 105 g (0.49 mole) of 1,4-dibromobutane in 500 ml of THF, was added a solution of 50 g (0.21 mole) of *sym*-tetraethoxydimethyldisilane[1] in 100 ml of THF with cooling in an ice bath, over 20 min. After 8-h reflux, part of the solvent (*ca.* 400 ml) was removed and the residue was decomposed with saturated aqueous solution of ammonium chloride. The organic layer was worked up and then fractionally distilled to afford 26 g (62% yield) of (III). The IR spectrum showed a group of absorption bands at 1080, 1025 and 1030 cm^{-1} characteristic of the silacyclopentyl group. The ^1H NMR spectrum (τ values) exhibited 9.87 ($SiCH_3$), 9.0-9.7 (CH_2, α to Si), and 8.2-8.5 (CH_2, β to Si).

Reaction of (I)

With perbenzoic acid

To 0.4 g (2.0 mmole) of *cis*-(I) was added a solution of perbenzoic acid (3.1 mmole) in 8 ml of methylene chloride. An exothermic, violent reaction occurred. After standing overnight, the solvent was evaporated. The remainder was diluted with ether and washed repeatedly with saturated aqueous solution of sodium bicarbonate, and the solvent was removed. Preparative GLC afforded *cis*-1,6-dimethyl-11-oxa-1,6-disilabicyclo[4.4.1]undecane (IV). The IR spectrum showed an intense band at 992 cm^{-1} owing to the siloxane bond.

The reaction of *trans*-(I) with the peracid was carried out in the similar manner, but was not so exothermic. After standing overnight at room temperature, GLC analysis showed that the reaction was completed and the sole product was the *cis* isomer of the siloxane (IV) (Found: C, 56.08; H, 10.11%). The retention time and the IR spectrum were exactly consonant with those of *cis*-(IV) obtained from *cis*-(I). The yields, estimated by GLC from runs employing a hydrocarbon added as a standard substance,

were 97% from *cis*-(I) and 83% from *trans*-(I).

With bis(trimethylsilyl) peroxide

cis-(I) (0.17 g; 0.85 mmole) was heated with bis(trimethylsilyl) peroxide[10] (0.36 g; 2.0 mmole) in a small sealed glass tube at 80° for 62 h. By GLC analysis, the reaction was complete and *cis*-(IV) was the sole product, in addition to hexamethyldisiloxane having arisen from the peroxide. The former (IV) had the retention time on GLC and the IR spectrum identical with those of an authentic sample.

trans-(I) was similarly reacted with the peroxide to give the *cis* isomer alone of (IV), which was identified by comparison of the retention time on GLC and the IR spectrum with an authentic sample. Removal of the volatile product left a viscous liquid polysiloxane (by IR spectrum). The yield of (IV) was 98% from *cis*-(I) and 22% from *trans*-(I)

With oxygen

The crystals (0.1 g) of *trans*-(I) were allowed to stand under oxygen atmosphere at room temperature for 20 days. After 5 days, the crystals in part changed oily and after 20 days, about 20 ml of oxygen was absorbed with leaving a viscous liquid. The only product detectable by GLC was *cis*-(IV), whose IR spectrum was superimposable upon that of the authentic sample. In striking contrast, *cis*-(I), even after oxygen was bubbled through the neat liquid at room temperature for 5 days, did not absorb oxygen at all. GLC analysis only showed the presence of the starting material.

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CHAPTER FOUR

PREPARATION AND CHARACTERIZATION OF 1,6-DISILA[4.4.4] PROPELLANE AND RELATED COMPOUNDS. EVIDENCE FOR A TRIALKYLSILYLMAGNESIUM COMPOUND

SUMMARY

The reaction of 9,10-dichloro-9,10-disiladecalin with $ClMg(CH_2)_4MgCl$ in tetrahydrofuran gave the title compound (4% yield) along with 10-butyl-5,10-disilaspiro[4.9]tetradecane (12% yield). Strong evidence has been obtained for the latter product having arisen from a silicon-magnesium compound formed as a fairly stable species. The disilapropellane absorbs ultraviolet light at 212 mμ.

INTRODUCTION

This chapter concerns the preparation of 1,6-disilatricyclo[4.4.4.$0^{1,6}$]-tetradecane (V), hereafter named 1,6-disila[4.4.4]propellane according to the "propellane" nomenclature[1]

In preceding chapters (2 and 3), it was mentioned that a substantial amount of strain is involved in a silicon-silicon containing six-membered heterocycle. Indeed, inspection of molecular models reveals that the tricyclic compound (V) is highly strained. However, it may become strain-free if both the silicon atoms assume trigonal bipyramidal configuration with either of them coinciding with an apical position of the other bipyramid (Fig. 1). This shape of the molecule will provide each silicon atom with a vacant,

relatively low energy orbital available for the attack of an electron-donating agent.

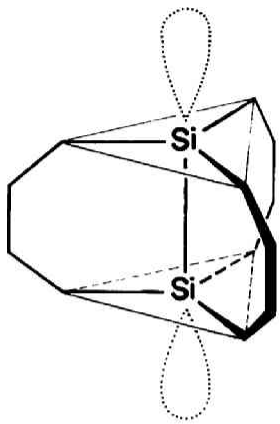


Fig. 1 A strain-relieved model of 1,6-disila[4.4.4]propellane with two trigonal-bipyramidal silicon atoms.

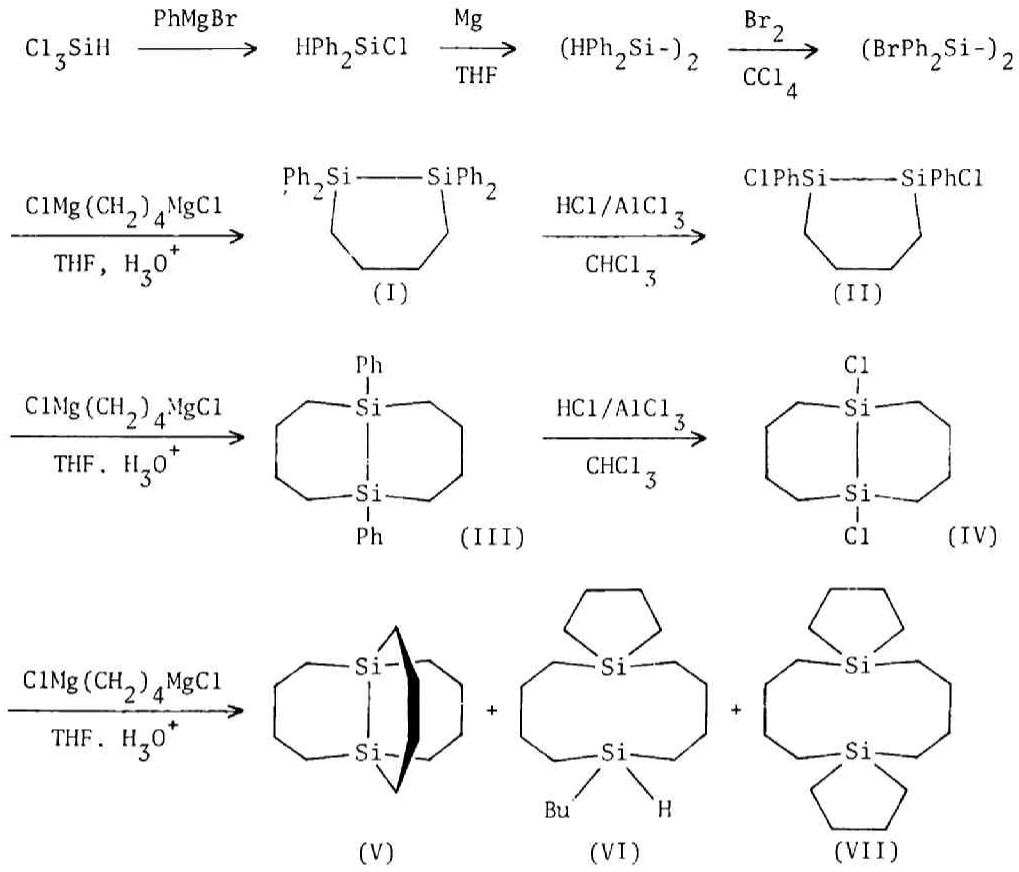
RESULTS AND DISCUSSION

The preparative route is summarized in Scheme 1, and new compounds together with their physical properties and analytical data are listed in Table 1.

1,1,2,2-Tetraphenyl-1,2-disilacyclohexane (I), which has been reported as unpublished work by Gilman *et al.*[2], and its precursors were prepared by the reported methods[3,4] 1,2-Dichloro-1,2-diphenyl-1,2-disilacyclohexane (II) was prepared in 76% yield by aluminum chloride catalyzed chlorodephenylation of (I) by hydrogen chloride in chloroform at room temperature. This reaction proceeded with cleavage of only one phenyl group from each silicon atom.

9,10-Diphenyl-9,10-disiladecalin (III) was obtained in 76% yield from (II) by treatment with the di-Grignard reagent from 1,4-dichlorobutane in tetrahydrofuran (THF). The product was homogeneous by GLC whereas analogously prepared *cis*- and *trans*-9,10-dimethyl-9,10-disiladecalin (VIII) were distinguishable (Chapter 3). As described in Chapter 3, the ^{1}H NMR spectrum

SCHEME 1



of *cis*-(VIII) shows two distinct groups of multiplet bands due to the ring methylene hydrogens whereas that of *trans*-(VIII) exhibits a much more complex pattern (see Fig. 1 in Chapter 3). In view of the NMR spectrum of (III) where the methylene hydrogen resonances appear in two discrete groups of multiplets (Fig. 2), it may have the *cis* configuration.

Chlorodephenylation of (III) by hydrogen chloride in the presence of aluminum chloride in chloroform gave 9,10-dichloro-9,10-disiladecalin (IV) in 89% yield.

Isomer ratios in compounds (II) and (IV) are not clear, because,

despite they were both homogeneous by GLC, upon methylation a mixture of *cis* and *trans* isomers was obtained in either case, *i.e.*, known *cis*- and *trans*-1,2-diphenyl-1,2-dimethyl-1,2-disilacyclohexane (Chapter 2) in the ratio of *ca.* 6 : 1 from (II) while *cis*- and *trans*-(VIII) (Chapter 3) in the ratio of *ca.* 3 : 1 from (IV).

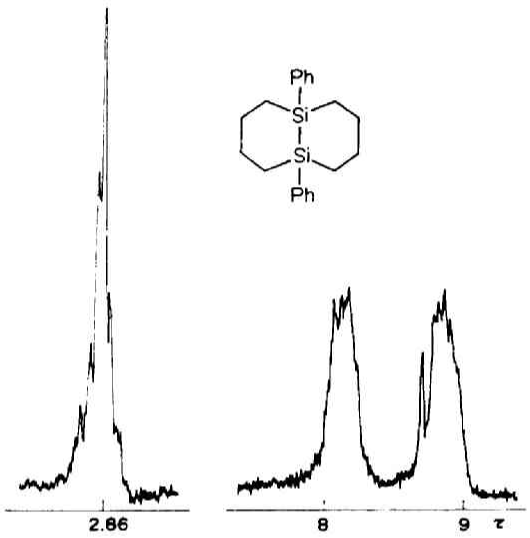


Fig. 2 ^{1}H NMR spectrum of 9,10-diphenyl-9,10-disiladecalin in carbon tetrachloride at room temperature (60 Mc).

The reaction of compound (IV) with tetramethylenedimagnesium dichloride in THF afforded mainly non-volatile, polymeric material (*ca.* 70%). However, from the volatile fraction consisting of several products, we could isolate by preparative GLC 1,6-disila[4.4.4]propellane (V) in 4% yield, together with 10-butyl-5,10-disilaspiro[4.9]tetradecane (VI) in 12% yield, and possibly 5,10-disiladispiro[4.4.4.4]octadecane (VII) in 3% yield, in the pure state.

Compound (V) is stable in air, whose NMR spectrum at room temperature shows two groups of multiplets due to methylene hydrogens (Fig. 3). It has an UV absorption maximum at 211.5 mμ in cyclohexane

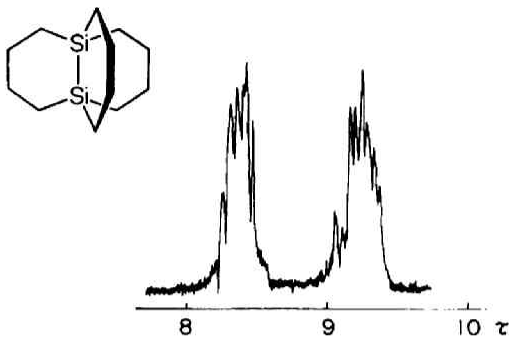
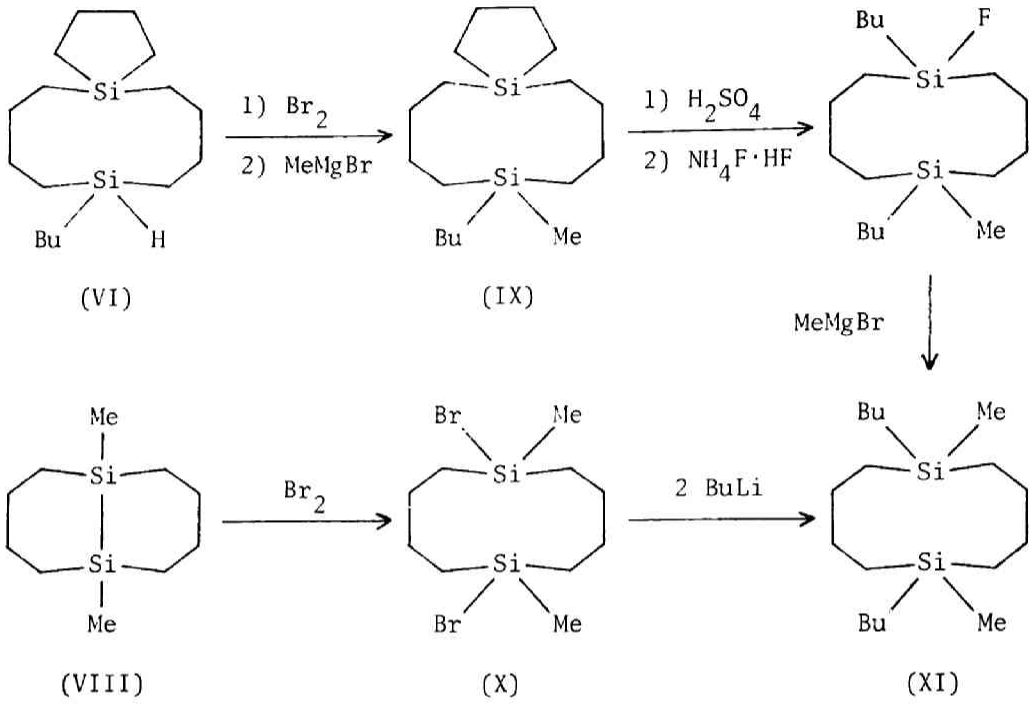


Fig. 3 ^{1}H NMR spectrum of 1,6-disila[4.4.4]propellane in carbon tetrachloride at room temperature (60 Mc).

(ϵ 7,700) and acetonitrile (ϵ 7,100) showing a bathochromic shift of some 20 mμ from hexamethyldisilane (near 198 mμ, ϵ 8,500-7,230[5] or 193.5 mμ, ϵ 10,800[6]). This absorption may be attributed to either the destabilization of the ground state due to the internal strain involved in the molecule or the appearance of low lying vacant level(s) owing to the rehybridization involving *d* orbitals which may occur in order to reduce the ring strain as mentioned above, or to both of these two effects. However, details will not be discussed in this thesis, since the absorption properties of related cyclic compounds must be investigated.

The presence of the silacyclopentane ring(s) in compounds (VI) and (VII) was established by a group of absorption bands in the IR spectra characteristic of such a ring, for which Nametkin *et al.*[7] reported a medium band at 1075 and a weak doublet at 1030 and 1020 cm^{-1} The IR spectrum of (VI) showed also the intense absorption of ν(Si-H) at 2090 cm^{-1} and its NMR spectrum displayed a multiplet resonance near τ 6.3 due to a hydrogen linked to silicon in addition to multiplets due to the ring methylene hydrogens. Crucial evidence for the structure of (VI) could be obtained by converting it into 1,6-dibutyl-1,6-dimethyl-1,6-disilacyclodecane (XI), an authentic sample of which was prepared independently from 9,10-dimethyl-9,10-disiladecalin (VIII) (Scheme 2).

SCHEME 2



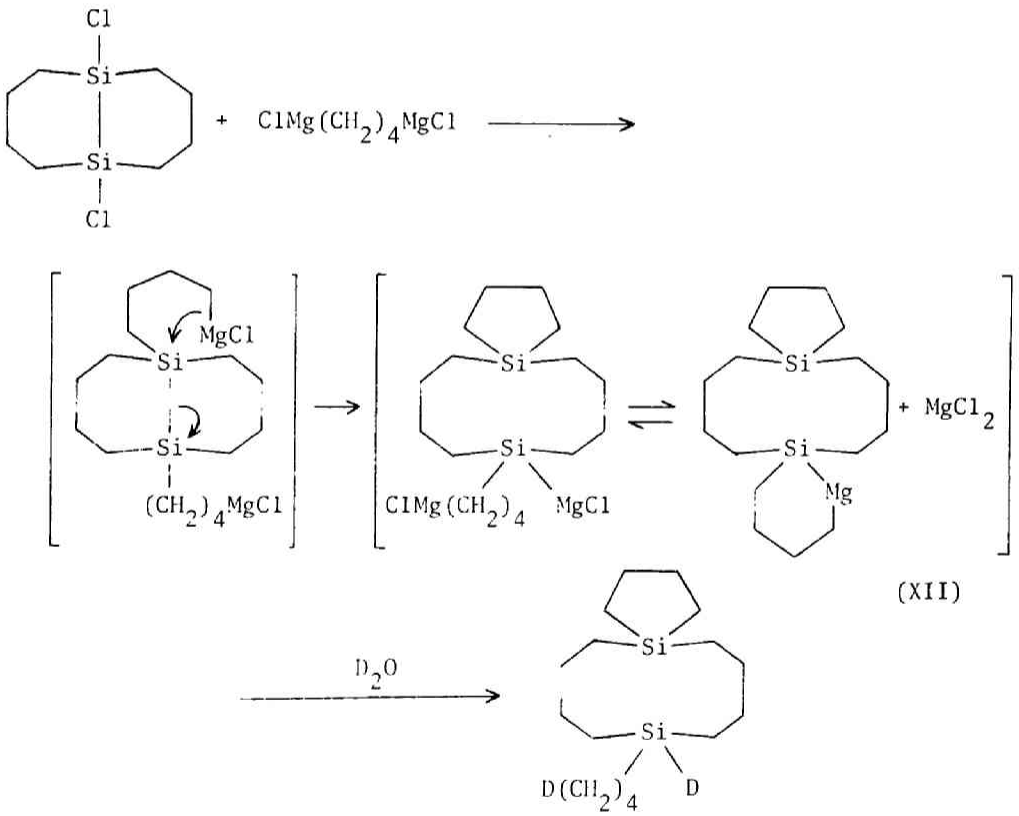
(VI) (IX) (VIII) (X) (XI)

Compound (VI) reacted with one equivalent of bromine with evolution of hydrogen bromide to give, after treatment with methylmagnesium bromide, 10-butyl-10-methyl-5,10-disilaspiro[4.9]tetradecane (IX), survival of the silacyclopentane ring being again shown by the IR spectrum. The action of concentrated sulfuric acid on (IX), as well-known[8], invoked fission of the five-membered ring, and successive treatments with ammonium hydrogen fluoride and with a methyl Grignard reagent led to compound (XI). Its IR spectrum showed that tl silacyclopentane ring was no longer present.

The production of (VI) may suggest that a trialkylsilylmagnesium compound is formed from cleavage of the silicon-silicon bond by the action of the Grignard reagent, which leads to the observed Si-H compound upon hydrolysis. In fact, work-up of the reaction mixture with deuterium oxide

in place of water afforded a dideuterated counterpart of compound (VI) containing one Si-D and one C-D bond on the terminal carbon atom of the butyl group (Scheme 3). Structure proof came from IR studies showing the appearance of the Si-D stretching frequency at 1525 cm^{-1} and the weak C-D stretching at 2175 cm^{-1} at the cost of the disappearance of the intense band at 2090 cm^{-1} due to the Si-H stretching and the weak peak at 1380 cm^{-1} due to symmetric deformation of the terminal methyl group. The NMR spectrum also revealed no proton resonance near τ 6.3.

SCHEME 3



The intermediate formation of silyl Grignard reagents has thus far been postulated in several times[9], for example, in the coupling of triphenylchlorosilane

to hexaphenyldisilane by cyclohexylmagnesium bromide in THF[10], in the synthesis of disilanes from aryl-containing monohaloorganosilanes with magnesium in THF[3], for the formation of dimethylphenylsilane from the action of methylmagnesium iodide on pentaiodopentaphenylcyclopentasilane, $(PhISi)_5$, in benzene/ether[11], and in other cases[12-15] It is generally recognized that aromatic groups on silicon can stabilize silyl anions and appear necessary for the formation of organosilylalkali compounds[16] and silyl Grignard reagents[10] To our knowledge, the silyl Grignard reagent (XII) is the first fully substantiated case of so stable a silicon-magnesium bond as to survive even under reflux conditions of THF despite the silicon atom linking to magnesium bears only alkyl groups but no aryl ones.

TABLE 1

Physical Properties and Analytical Data for New Compounds

Compound		M.p. (°C)	B.p. (°C/mm)	C(%)	H(%)
				Found (Calcd.)	Found (Calcd.)
$C_{16}H_{18}Cl_2Si_2$	(II)	68-69.5	148-151/0.03	56.77(56.96)	5.61(5.38)[a]
$C_{20}H_{26}Si_2$	(III)	104-105	*ca.* 188-190/4	74.45(74.46)	8.34(8.12)
$C_8H_{16}Cl_2Si_2$	(IV)	29.5-31.0	90/4	40.07(40.15)	6.85(6.74)[b]
$C_{12}H_{24}Si_2$	(V)	114-115.5	---	64.41(64.20)	10.92(10.78)
$C_{16}H_{34}Si_2$	(VI)	---	124-126/1[c]	67.74(68.00)	12.10(12.12)
$C_{16}H_{32}Si_2$	(VII)	89.5-90.5	---	68.69(68.49)	11.38(11.49)
$C_{17}H_{36}Si_2$	(IX)	---	124-126/1	69.13(68.83)	12.24(12.23)
$C_{10}H_{22}Br_2Si_2$	(X)	105-109	118-122/1	33.86(33.52)	6.22(6.19)[d]
$C_{18}H_{40}Si_2$	(XI)	---	132-134/2[e]	69.30(69.14)	12.84(12.89)

[a] Cl, 21.39(21.02). [b] Cl, 29.98(29.63). [c] n_D^{20} 1.5050, d_4^{20} 0.9207; MR_D Found 91.05, calcd. 91.32. [d] Br, 45.38(44.61). [e] n_D^{20} 1.4834, d_4^{20} 0.8785; MR_D Found 101.72, calcd. 102.35.

EXPERIMENTAL

All reactions were carried out under nitrogen atmosphere. Diphenylchlorosilane was prepared in about 65% yield by adding phenylmagnesium bromide in ether to a solution of trichlorosilane in benzene. *sym*-Tetraphenyldisilane and *sym*-tetraphenyldibromodisilane were synthesized as described in refs. 3 and 4. Infrared spectra were measured on a Hitachi EPI-G3 grating spectrophotometer. NMR spectra were obtained on a JEOL Model C-60H spectrometer in carbon tetrachloride solution with benzene or TMS as an internal standard. UV spectra were measured on a Hitachi EPS-3T spectrophotometer. Molecular weights were obtained from mass spectra measured on a Hitachi RMS-4 mass spectrometer. A Varian Aerograph Model 90P, equipped with a 20 ft column packed with Apiezon-L (20% on Celite), was used for isolation and purification.

1,1,2,2-Tetraphenyl-1,2-disilacyclohexane (I)

In a 2-l three-necked flask, equipped with a reflux condenser, a stirrer and a pressure-equalizing addition funnel, was prepared a Grignard solution from 22.9 g (0.18 mole) of 1,4-dichlorobutane, 10.5 g (0.43 g-atom) of magnesium and 200 ml of THF. After 4-h reflux, the solution was diluted with THF up to 1.7 l. A solution of 52.4 g (0.10 mole) of *sym*-tetraphenyldibromodisilane in 300 ml of THF was added with stirring at room temperature over a period of 4 h. After the addition was completed, the reaction mixture was refluxed for 65 h. Solvent was removed by distillation and the remainder was hydrolyzed with dilute hydrochloric acid. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and saturated solution of sodium bicarbonate, and dried over potassium carbonate. After removal of solvents, volatile materials were evaporated under reduced pressure up to 60°/6 mm. Recrystallization of the remaining mass from ethanol (*ca.* 300 ml) gave 32 g (76% yield) of (I) as white needle crystals, m.p. 109 - 110° (lit.[2] 110 - 111°). A second run carried out in essentially the same way, except for a shorter reflux period of 18 h, resulted in a slightly poorer yield (68%). Use of 1,4-dibromobutane in place of the chloride also led to poorer yield (52%)

1,2-Diphenyl-1,2-dichloro-1,2-disilacyclohexane (II)

In a 500 ml three-necked flask, equipped with a gas inlet tube, a stirrer and a reflux condenser the top of which was protected with a drying tube, was placed a mixture of 42.1 g (0.10 mole) of compound (I), 500 ml of chloroform and 2.0 g of aluminum chloride. Into the stirred mixture was passed dry hydrogen chloride at room temperature. Slightly exothermic reaction occurred. The extent of the reaction was monitored by GLC analysis (Apiezon-L, 10% on Celite 545 at 290-300°) of small samples extracted periodically from the reaction mixture. After about 12 h, the starting substance disappeared with the formation of a single product homogeneous by GLC. At this point the introduc-

tion of hydrogen chloride was discontinued and *ca.* 10 ml of acetone was added to the mixture for the purpose of deactivating the catalyst. After standing overnight, acetone-aluminum chloride complex was removed by filtration. Removal by distillation of the solvent and benzene produced during the reaction, followed by distillation of the residue through a short Vigreux column gave 25.5 g (75.5% yield) of (II) as a brown crystallizable material. The colored product was pure enough for the purpose of the next cyclization reaction and used without any further purification.

The colored matter (25.5 g) was dissolved in 50 ml of dry hexane and treated with activated carbon at 40-50° for 2 h. After filtration, the filtrate was cooled at -20 to -30° for about 5 h, giving 12 g (36%) of the colorless product.

9,10-Diphenyl-9,10-disiladecalin (III)

The reaction was carried out in essentially the same manner as described in the preparation of compound (I) except for use of 33.7 g (0.10 mole) of compound (II) in place of *sym*-tetraphenyldibromodisilane and 6 days' reflux of the reaction mixture. Work-up and subsequent recrystallization from ethanol (*ca.* 350 ml) afforded 24.5 g (76% yield) of compound (III) as white cubic crystals. GLC (Apiezon-L, 10% on Celite 545, 8 ft, at 280°) showed a single peak, indicating that the product contained only one isomer of *cis* and *trans* isomers, since the two isomers of its methyl analog, *i. e.* 9,10-dimethyl-9,10-disiladecalin (VIII), were distinguishable on the same column. In the light of the whole pattern of the NMR spectrum due to methylene hydrogens which fell into two groups, the product was considered to be the *cis* isomer.

9,10-Dichloro-9,10-disiladecalin (IV)

In a similar manner to that described in the preparation of compound (II), 20 g (0.062 mole) of (III) in 100 ml of chloroform was chlorodephenylated in the presence of *ca.* 1 g of aluminum chloride by passing dry hydrogen chloride at room temperature for 10 h. Work-up in the usual way and subsequent distillation gave 13.1 g (89% yield) of (IV) boiling mainly at 90°/5 mm. The colorless product thus obtained was homogeneous by GLC and crystallized upon cooling.

Methylation of (II)

To 5.0 g (14.8 mmole) of (II), purified by recrystallization from *n*-hexane, was added a large excess of methylmagnesium bromide (*ca.* 100 mmole) in ether (70 ml). After reflux for 4 h, the mixture was worked up and distilled to give 3.8 g (87% yield) of 1,2-diphenyl-1,2-dimethyl-1,2-disilacyclohexane, b.p.178-183°/7 mm, as a 6 : 1 mixture of *cis* and *trans* isomers.

Methylation of (IV)

Compound (IV) (0.24 g; 1 mmole), which was homogeneous by GLC, was allowed to react with excess methylmagnesium bromide in ether/THF solvent. After 30-h reflux, and subsequent hydrolysis, GLC analysis of the resulting organic layer showed the formation of a *cis* and *trans* mixture (3 : 1) of 9,10-dimethyl-9,10-disiladecalin.

Reaction of (IV) with $ClMg(CH_2)_4MgCl$ in THF

In essentially the same manner as described in the preparation of compound (I), 12 g (0.05 mole) of 9,10-dichloro-9,10-disiladecalin (IV) was reacted with a Grignard reagent prepared from 11.4 g (0.09 mole) of 1,4-dichlorobutane and 5.3 g (0.218 g-atom) of magnesium in 1 l of THF The reaction mixture was refluxed for 5 days. Work-up followed by distillation gave two fractions; (1) b.p. up to 170°/5 mm, 1.7 g and (2) b.p. 170-175°/5 mm, 3.9 g, leaving 8.0 g of nonvolatile viscous residue. A major product in the fraction (1) was isolated by preparative GLC (280°). The crystals (0.45 g, 4% yield) thus obtained were recrystallized from methanol and then ethanol, and identified as 1,6-disilatricyclo[4.4.4.$0^{1,6}$]tetradecane (V) (mol. wt.: Found 224; $C_{12}H_{24}Si_2$ calcd. 224.50). A major product in the fraction (2) was isolated as a colorless liquid (1.7 g, 12% yield) by preparative GLC (280°) and was identified as 10-butyl-5,10-disilaspiro[4.9]tetradecane (VI) (mol. wt.: Found 282; $C_{16}H_{34}Si_2$ calcd. 282.63). The IR spectrum indicated the presence of the Si-H bond (2090 cm^{-1}) and the silacyclopentane ring (1027, 1033 and 1080 cm^{-1}). A minor product isolated from the fraction (2) was recrystallized from ethanol (0.4 g, 3% yield) and identified as 5,10-disiladispiro[4.4.4.4] octadecane (VII) (mol. wt.: Found 280; $C_{16}H_{32}Si_2$ calcd. 280.61).

Reaction of (VI) with bromine followed by methylation

To a solution of 1.6 g (5.7 mmole) of (VI) in 10 ml of carbon tetrachloride was added dropwise a solution of bromine (0.9 g; 5.7 mmole) in 10 ml of carbon tetrachloride with cooling in an ice bath, under vigorous stirring. The red color immediately disappeared with evolution of hydrogen bromide. Addition of slight excess bromine caused to leave the red color, indicating the presence of only one Si-H bond and the absence of Si-Si bond in the starting material. The solvent was evaporated at reduced pressure, and the remaining viscous oil was treated with a large excess of methylmagnesium bromide in ether (*ca.* 50 mmole). After 3-h reflux, the reaction mixture was worked up in the usual way and then distilled to give a colorless liquid (IX, 1.2 g) boiling mainly at 124-126°/1 mm, which was homogeneous by GLC. The IR spectrum was almost identical with that of the starting material except for the disappearance of the absorption at 2090 cm^{-1} [ν(Si-H)] and the appearance of a strong band at 1250 cm^{-1} indicative of the presence of the $Si-CH_3$ group.

Reaction of compound (IX) with concentrated sulfuric acid followed by treatment with ammonium hydrogen fluoride and then with a methyl Grignard reagent

A mixture of 1.0 g of (IX) diluted with benzene (15 ml) and 30 g of concentrated sulfuric acid was stirred vigorously at 25-30° The extent of the reaction was followed by GLC analysis of small samples extracted from the organic layer. After 15 h, the starting material disappeared from the organic phase. At that point, under cooling in an ice bath, 5 g (0.088 mole) of ammonium hydrogen fluoride was added in several portions. GLC analysis of the resulting organic layer showed the formation of a product different from the starting material, together with two products in small amounts. The organic layer and extracts (benzene 30 ml) from the acid layer were combined and the solvent was removed by distillation. To the remaining oil was added a large excess of methylmagnesium bromide in ether (*ca.* 50 mmole). Work-up, distillation (0.9 g, up to 140°/2 mm) and subsequent purification by preparative GLC afforded 0.2 g of (XI), its IR and NMR spectra and the retention time on GLC being identical with those of the authentic sample, prepared below.

1,6-Dibromo-1,6-dimethyl-1,6-disilacyclodecane (X)

To a solution of 6.0 g (30 mmole) of 9,10-dimethyl-9,10-disiladecalin (VIII; *cis/trans* mixture) in 30 ml of carbon tetrachloride was added a solution of 4.8 g (30 mmole) of bromine in 20 ml of carbon tetrachloride with cooling in an ice bath. The red color immediately disappeared. After removal of carbon tetrachloride by distillation, the reaction mixture was distilled to give 7.0 g (66%) of (X) as white crystals.

1,6-Dibutyl-1,6-dimethyl-1,6-disilacyclodecane (XI)

A solution of butyllithium in hexane (60 mmole) was added to a solution of 6.3 g (17.6 mmole) of 1,6-dibromo-1,6-dimethyl-1,6-disilacyclodecane (X) in 50 ml of ether in the cold over 20 min and the mixture was stirred at room temperature for 5 h. After hydrolysis with dilute hydrochloric acid and subsequent work-up in the usual way, distillation at reduced pressure gave 5.0 g (91% yield) of (XI) in a slightly impure state. Repeated distillation afforded a pure sample boiling mainly at 132-134°/2 mm.

Reaction of (IV) with $ClMg(CH_2)_4MgCl$, followed by treatment with deuterium oxide

Compound (IV) (1.6 g; 6.7 mmole) was added to an excess of the Grignard reagent, prepared from 6.3 g (49.6 mmole) of 1,4-dichlorobutane and 3.0 g (123.4 mg-atom) of magnesium in 400 ml of THF After reflux for 8 h, the reaction mixture was treated with 8.0 g (0.4 mole) of deuterium oxide. The resulting salt and excess magnesium were filtered and washed with 200 ml of ether. The organic layer was distilled to give 0.5 g of a liquid boiling over the range of 100-140°/2 mm, leaving 1.2 g of residue. From the above fraction a product with the same retention time on GLC as that of

compound (VI) was isolated by preparative GLC and identified as 10-deutero-10-(4-deuterobutyl)-5,10-disilaspiro[4.9]tetradecane (mol. wt.: Found 284; $C_{16}H_{32}D_2Si_2$ calcd. 284.63). In the IR spectrum, two new peaks were observed to appear at 2175 cm^{-1} (w.) and 1525 cm^{-1} (s.) owing to ν(C-D) and ν(Si-D), respectively, with almost disappearance of an intense band at 2090 cm^{-1} due to ν(Si-H) and of a weak peak at 1380 cm^{-1} due to symmetric deformation of the terminal methyl group. The pattern of other part of the spectrum was essentially the same as that of (VI). The ^1H NMR spectrum also revealed the absence of the silicon-hydrogen bond, since no signals occurred near τ 6.3.

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PART TWO

(Halomethyl) disilanes

CHAPTER FIVE

REACTIONS OF (CHLOROMETHYL)PENTAMETHYLDISILANE WITH SOME NUCLEOPHILIC REAGENTS

SUMMARY

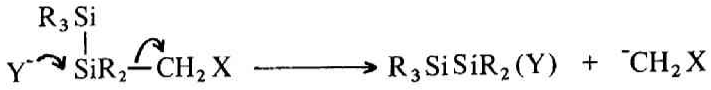
(Chloromethyl)pentamethyldisilane (I) underwent predominantly intramolecular rearrangement when treated with sodium methoxide, isopropoxide and phenoxide to give the corresponding alkoxypentamethyldisilylmethanes $(CH_3)_3SiCH_2Si(CH_3)_2OR$, whereas it gave only substitution products of the formula $(CH_3)_3SiSi(CH_3)_2CH_2Y$ when allowed to react with sodium ethylmercaptide and thiophenolate, and with diethylamine and aniline. The reaction of (I) with potassium acetate in acetic acid proceeded in two steps: first, substitution; second, intramolecular rearrangement of the substitution product. Three organo-functional organodisilanes, viz. (acetoxymethyl)-, (methoxymethyl)- and (cyanomethyl)pentamethyldisilane, which could not be obtained by the nucleophilic substitution, were prepared by alternative methods and some of their reactions studied.

INTRODUCTION

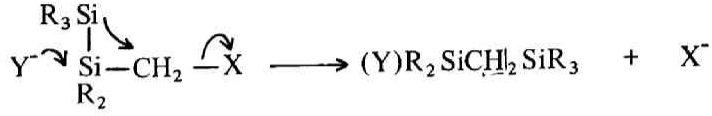
(Halomethyl)disilanes contain three centers on which attack by nucleophilic reagents can occur; *i.e.* the halomethyl carbon and two silicon atoms. Consequently, there are five *a priori* possible reaction courses.

(A) Substitution of the halogen atom (attack on the carbon).

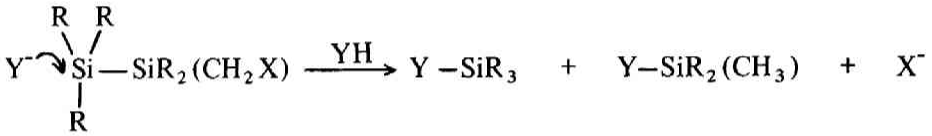
(B) Cleavage of the silicon-carbon bond (attack on the α–silicon*).



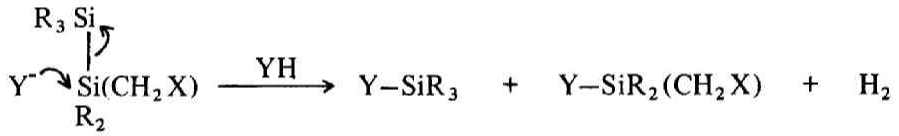
(C) Intramolecular rearrangement of a silyl group from silicon to carbon (attack on the α–silicon).



(D) Cleavage of the silicon-silicon bond without evolution of hydrogen but with concomitant reduction of the halomethyl to methyl group (attack on the β–silicon).



(E) Cleavage of the silicon-silicon bond with evolution of hydrogen keeping the halomethyl group intact (attack on the α–silicon).



Not only the nature of the reagent used but also the nature and the position of the substituents on silicon atom may govern these directions. Kumada and Ishikawa reported[1] that (chloromethyl)pentamethyldisilane $ClCH_2(CH_3)_2SiSi(CH_3)_3$ (I) selectively undergoes three different types of nucleophilic reactions. Thus, by iodide ion in acetone, substitution of the chlorine atom took place to give (iodomethyl)pentamethyldisilane; ethoxide ion in ethanol caused intramolecular rearrangement to give ethoxypentamethyldisilylmethane; while cyanide ion in ethanol gave cleavage of the silicon-carbon bond to yield ethoxypentamethyldisilane. As an extention of their work we have studied the reactions of compound (I) with further several nucleophilic reagents.

*The silicon atom bearing a halomethyl group is designated the α–silicon, and the other is the β–silicon.

In this chapter we discuss mainly the first three courses (A)–(C). The last two courses (D) and (E) will be discussed in Chapter 8, because the cleavage of the silicon-silicon bond becomes remarkable in (halomethyl)disilanes containing groups other than methyl on silicon, as will be described in Chapters 6 and 7.

RESULTS AND DISCUSSION

As nucleophilic reagents, we selected the following systems: CH_3ONa–CH_3OH, iso-C_3H_7ONa–iso-C_3H_7OH, *tert*-C_4H_9ONa–*tert*-C_4H_9OH, C_6H_5ONa–C_6H_5OH, C_2H_5SNa–C_2H_5SH, C_6H_5SNa–C_6H_5SH, $(C_2H_5)_2NH$, $C_6H_5NH_2$, and CH_3CO_2K–CH_3CO_2H. The reaction mixture was heated either in a sealed glass tube or in a flask at an ordinary pressure for a given period of time. Sometimes, the reaction was followed by gas chromatography. Structure proof for the reaction products was based on their infrared spectra as well as their behavior towards bromine. As has been reported recently by Fritz *et al.*[2], the infrared spectra of compounds with $SiCH_2Si$ structure exhibit a band near 1050 cm^{-1} assignable to the deformation vibration of the C–H bond of this group, while those of $SiSiCH_2$ compounds do not. Compounds containing the silicon–silicon bond react with bromine violently in the cold, whereas compounds with the $SiCH_2Si$ structure, in general, do not. Of course, this test is invalid, if the compound contains any group (for instance, NHC_6H_5) as sensitive as the silicon–silicon bond to the action of bromine.

We now find that (I) reacts with sodium ethoxide in ethanol to form preferentially the rearrangement product, $(CH_3)_3SiCH_2Si(CH_3)_2OEt$ together with about 30% of trimethylethoxysilane resulting from cleavage of the silicon-silicon bond in the fashion depicted by course (D) (see Chapter 8). Similarly, the predominant formation of rearrangement products, $(CH_3)_3SiCH_2Si(CH_3)_2OR$ (II, R=CH_3; III, R=iso-C_3H_7; IV, R=C_6H_5), was observed when methoxide, isopropoxide and phenoxide reagents were used. In the case of *tert*-butoxide, the starting substance (I) was recovered unchanged even on heating in a sealed tube at 150° for 125 h. Doubtless, this is because of steric hindrance.

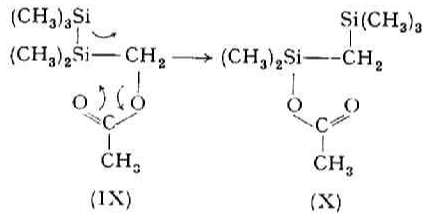
With the mercaptides and the amines, only substitution products $(CH_3)_3SiSi(CH_3)_2CH_2Y$ (V, Y=SC_2H_5; VI, Y=SC_6H_5; VII, Y=$N(C_2H_5)_2$; VIII, Y=NHC_6H_5) were obtained as in the reaction with iodide ion, previously reported[1]

The reaction with acetate ion in acetic acid was found to proceed i-

two steps: first, substitution leading to the formation of (acetoxymethyl)pentamethyldisilane (IX); second, intramolecular rearrangement to give acetoxypentamethyldisilylmethane (X). Following the reaction by GLC revealed that the substitution product appeared about 1 h after heating was started, some amount of the rearrangement product was formed about 20 h later and the rearrangement was complete at the point of 117 h. In order to confirm the thermal intramolecular rearrangement of (acetoxymethyl)pentamethyldisilane, we prepared it by the reaction of (hydroxymethyl)pentamethyldisilane[3] with acetic anhydride.

$$(CH_3)_3SiSi(CH_3)_2CH_2OH + (CH_3CO)_2O \longrightarrow \underset{(IX)}{(CH_3)_3SiSi(CH_3)_2CH_2OOCCH_3} + CH_3COOH$$

Indeed, (acetoxymethyl)pentamethyldisilane (IX) was converted, under reflux conditions, into acetoxypentamethyldisilylmethane (X) in 6.5 h in bulk, but after several tens of hours in an acetic acid solution. It seems likely that the intramolecular rearrangement of compound (IX) will proceed *via* a cyclic transition state as shown below:



(IX) (X)

All attempts to prepare (methoxymethyl)pentamethyldisilane (XI) from $(CH_3)_3SiSi(CH_3)_2CH_2X$ (X=Cl, I) compounds failed. Thus, the reaction of (chloromethyl)pentamethyldisilane (I) with sodium methoxide in *n*-heptane as well as in ethyleneglycol dimethyl ether resulted only in the formation of the methoxypentamethyldisilylmethane (II). Treatment of (iodomethyl)pentamethyldisilane[1] with silver oxide in methanol also gave a rearrangement product, $[(CH_3)_3SiCH_2Si(CH_3)_2]_2O$. The successful preparation of the desired compound, however, was attained by the reaction of chloropentamethyldisilane with monochloromethyl ether in the presence of magnesium in tetrahydrofuran (THF), which is an application of the method recently disclosed in the patent literature[4]

$$(CH_3)_3SiSi(CH_3)_2Cl + ClCH_2OCH_3 \xrightarrow[THF]{Mg} (CH_3)_3SiSi(CH_3)_2CH_2OCH_3 \quad (XI)$$

It is noteworthy that the (methoxymethyl)pentamethyldisilane (XI), once prepared, was surprisingly stable to the action of methoxide and ethoxide ion. No change was detected by GLC analysis when the reaction mixture was subjected to conditions under which the formation of the alkoxypentamethyldisilylmethane from the reaction of (chloromethyl)pentamethyldisilane (I) with the alkoxide ion would be complete.

(Cyanomethyl)pentamethyldisilane (XII) was successfully prepared through the reaction of pentamethyldisilanylmethylmagnesium chloride with cyanogen, after the technique used by Prober[5] for the preparation of the corresponding monosilane compound.

$$(CH_3)_3SiSi(CH_3)_2CH_2MgCl + (CN)_2 \longrightarrow (CH_3)_3SiSi(CH_3)_2CH_2CN \quad (XII)$$

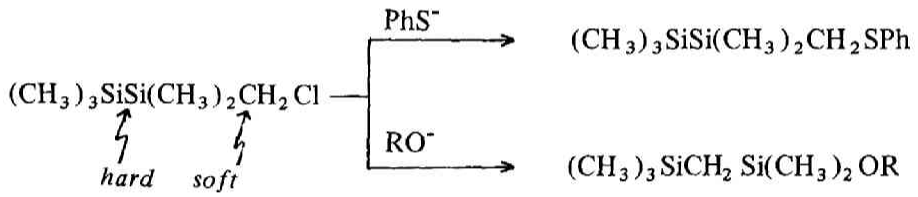
It was found that this compound was stable when refluxed in a pure ethanol solution, but underwent complete cleavage of the cyanomethyl group to give ethoxypentamethyldisilane when refluxed in ethanol containing a catalytic amount of cyanide ion.

$$(CH_3)_3SiSi(CH_3)_2CH_2CN + C_2H_5OH \xrightarrow{CN^-} (CH_3)_3SiSi(CH_3)_2OC_2H_5 + CH_3CN$$

From these observations it seems likely that the differences in thermodynamic stability between the rearrangement and substitution products formed in a given nucleophilic reaction of (chloromethyl)pentamethyldisilane (I) may be a major factor in determining the direction of the reaction. Thus, the relatively large difference in calculated bond energies (see *e.g.* ref. 6) between the structures $SiCH_2SiOR$ and $SiSiCH_2OR$ (49.1 kcal/mole) favors the formation of the rearrangement product, while only substitution products are formed in cases of iodide ion, mercaptide ions and amines because the corresponding bond energy differences are not very large: $SiCH_2SiI - SiSiCH_2I$ 27.0, $SiCH_2SiSR - SiSiCH_2SR$ 34.0, $SiCH_2SiNR_2 - SiSiCH_2NR_2$ 28.2 and $SiCH_2SiCN - SiSiCH_2CN$ 14.1 kcal/mole. Doubtless, easy cleavage of the cyanomethyl group from silicon in the presence of an anion is due to high electronegative nature of the CH_2CN group. A satisfactory explanation of the observed high stability of $(CH_3)_3SiSi(CH_3)_2CH_2OCH_3$, once formed, to intramolecular rearrangement, of course, is not given by the simple considerations on the basis of bond energy calculation.

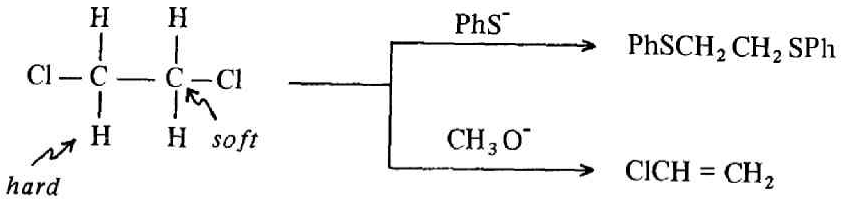
The principle of "Hard and Soft Acids and Bases", which has recently been discussed in detail by Pearson[7], seems applicable to explain our results. The rule states that soft bases prefer to bind to soft acids and hard bases to

hard acids. Electronically saturated centers are typical soft acids and are predicted to interact with soft bases. Of the nucleophiles used here, typical soft bases, I^-, RS^- and CN^-, tend to attack on the carbon atom of the chloromethyl group to give the substitution products. On the other hand, alkoxide ions which are typical hard bases react predominantly with the silicon center linking to the chloromethyl group to form the rearrangement products.



This means that, whereas electronically saturated centers are regarded as typical soft acids, the carbon atom of the chloromethyl group is soft but the silicon atom hard because of its electron deficiency owing to lower electronegativity (C, 2.5–2.6. Si, 1.8–1.9)[8]

It is interesting to compare the reaction courses of compound (I) with those of 1,2-dichloroethane upon treatment with nucleophiles[9]:



Formulas and some physical properties of the compounds prepared in the present study are listed in Table 1, and molar refractions and analytical data in Table 2.

TABLE 1

PHYSICAL PROPERTIES OF REACTION PRODUCTS FROM (CHLOROMETHYL)PENTAMETHYLDISILANE (I)

No.	*Formula*	*B.p.* (°C/*mm*)	n_D^{20}	d_4^{20}
(II)	$(CH_3)_3SiCH_2Si(CH_3)_2OCH_3$[a]	58/32	1.4170	0.8154
(III)	$(CH_3)_3SiCH_2Si(CH_3)_2O$-iso-$C_3H_7$	*ca.* 88/56	1.4190	0.8118
(IV)	$(CH_3)_3SiCH_2Si(CH_3)_2OC_6H_5$	86/3.5	1.4821	0.9134
(V)	$(CH_3)_3SiSi(CH_3)_2CH_2SC_2H_5$	94/18	1.4778	0.8523
(VI)	$(CH_3)_3SiSi(CH_3)_2CH_2SC_6H_5$	109/2	1.5419	0.9485
(VII)	$(CH_3)_3SiSi(CH_3)_2CH_2N(C_2H_5)_2$	82/15	1.4549	0.7986
(VIII)	$(CH_3)_3SiSi(CH_3)_2CH_2NHC_6H_5$	104/1.5	1.5247	0.9070
(IX)	$(CH_3)_3SiSi(CH_3)_2CH_2OOCCH_3$	72/14	1.4424	0.8774
(X)	$(CH_3)_3SiCH_2Si(CH_3)_2OOCCH_3$	80/21	1.4240	0.8837
(XI)	$(CH_3)_3SiSi(CH_3)_2CH_2OCH_3$	57/37	1.4342	0.7982
(XII)	$(CH_3)_3SiSi(CH_3)_2CH_2CN$	105/25[b]		

[a] Lit. 10, b.p. 148–152°, n_D^{25} 1.4120, d_4^{25} 0.813. [b] M.p. *ca.* 30°.

TABLE 2

MOLAR REFRACTIONS AND ANALYTICAL DATA

No.	MR_D		*C* %		*H* %	
	Found	*Calcd.*[a]	*Found*	*Calcd.*	*Found*	*Calcd.*
(II)	54.40	54.50	47.98	47.66	11.61	11.43
(III)	63.62	63.80	52.92	52.87	11.71	11.83
(IV)	74.45	74.55	60.18	60.43	9.38	9.30
(V)	68.56	68.40	46.25	46.53	10.46	10.74
(VI)	84.46	83.50	56.76	56.62	8.63	8.71
(VII)	73.88	73.56	55.09	55.22	12.50	12.51
(VIII)[b]	80.07	79.18	61.19	60.69	9.98	9.76
(IX)	61.69	62.07	47.27	47.00	9.63	9.86
(X)	59.09	59.04	47.43	47.00	10.27	9.86
(XI)	57.58	57.61	47.56	47.66	11.14	11.43
(XII)[c]	—	—	49.32	49.06	10.08	10.00

[a] See ref. 11. [b] N % found 5.89, calcd. 5.90. [c] N % found 8.60, calcd. 8.17.

EXPERIMENTAL

All temperatures reported here are uncorrected. (Chloromethyl)pentamethyldisilane (I) was prepared as reported previously[1]

Reactions of conpound (I)

(1) With CH_3ONa in CH_3OH. Sodium (2.1 g, 0.091 g-atom) was dissolved in 30 ml of absolute methanol in a 2.6 x 50 cm glass tube. To the solution was added 15 g (0.083 mole) of (I). The tube was flushed with nitrogen, sealed, and heated in an oil bath at 95–110° for 15 h. Ether was then used to transfer the contents of the opened tube to a flask, and the mixture neutralized cautiously by passing dry hydrogen chloride. The precipitate was filtered and washed with ether. The filtrate was combined with washings and fractionally distilled in a small column rated at about 20 theoretical plates to give 5.7 g (40 % yield) of gas–chromatographically homogeneous methoxypentamethyldisilylmethane (II). GLC analysis of the distillation residue showed the presence of $[(CH_3)_3SiCH_2Si(CH_3)_2]_2O$. Neither the distillate nor residue reacted with bromine. The IR spectrum of (II) showed significant bands at 1050 (C–H deformation in $SiCH_2Si$), 1094 (Si–O stretching) and 2830 cm^{-1} (C–H stretching in OCH_3).

(2) With CH_3ONa in $CH_3OCH_2CH_2OCH_3$. To a dispersion of methanol-free sodium methoxide (0.06 mole) in ethyleneglycol dimethyl ether (30 ml) was added 10 g (0.056 mole) of (I) at room temperature with stirring. Reaction set in with considerable evolution of heat, which required cooling. GLC analysis showed that the reaction was complete after 30 min, and the only product was methoxypentamethyldisilylmethane (II). Fractionation gave 6 g of (II).

(3) With CH_3ONa in n-heptane. This experiment was carried out in essentially the same manner as above except that 20 ml of *n*-heptane in place of ethyleneglycol dimethyl ether was used. It was necessary to continue stirring for 11 h to complete the reaction. Gas chromatography showed that the product was exclusively (II).

(4) With iso-C_3H_7ONa in iso-C_3H_7OH. In a similar glass tube to that used above, 10 g (0.056 mole) of (I) was allowed to react with 0.061 mole of sodium isopropoxide in isopropyl alcohol at 95–110° for 22 h, and the reaction mixture was worked up as above. Fractional distillation gave 4 g of isopropoxypentamethyldisilylmethane (III) contaminated with about 30% (by GLC) of the starting material. Preparative GLC gave a pure sample of (III) for analyses and measurements of physical properties. The product did not react with bromine. Its IR spectrum showed bands at 1050 (C–H deformation) and 1026 cm^{-1} (Si–O stretching).

(5) With C_6H_5ONa. Sodium phenoxide was prepared from 18 g (0.19 mole) of phenol and 5.2 g (0.13 mole) of sodium hydroxide dissolved in a small amount of water. To this mixture was added 500 ml of benzene; water was then removed completely together with benzene by distillation, initially at atmospheric pressure, later *in vacuo*. Compound (I) (20 g, 0.11 mole) was added to the residue and heated to reflux with stirring for 70 h. The precipitate was filtered off, and the filtrate was fractionally distilled to give 13 g (43 % yield) of phenoxypentamethyldisilylmethane (IV). It reacted with bromine as easily as phenol, but not as violently as any disilane derivative did. A small sample of the product was shaken with dilute hydrochloric acid, and a ferric chloride solution was added to it. The test for phenol was positive. The IR spectrum of (IV) showed bands at 1050 (C–H deformation) and 1030 cm^{-1} (Si–O stretching).

(6) With C_2H_5SNa in C_2H_5SH. A mixture of 15 g (0.083 mole) of (I) and sodium ethylmercaptide prepared from 2.1 g (0.091 g-atom) of sodium in 30 g (0.48 mole) of ethanethiol was heated in a 2.6 x 50 cm sealed glass tube at 95–110° over a period of 83 h. The contents of the reaction tube were filtered and flash-distilled. The salt-free distillate was redistilled in a column to give 13 g (76 % yield) of (ethylthiomethyl)-pentamethyldisilane (V). A sample of this compound did react violently with bromine in the cold. Its IR spectrum showed no band near 1050 cm^{-1}

(7) With C_6H_5SNa in C_6H_5SH. A mixture of 15 g (0.083 mole) of (I) and 15 g of thiophenol containing 0.09 mole of sodium thiophenolate was heated in a similar tube to that above at 95–110° for 57 h and then at 130–150° for 45 h. Fractionation of the organic layer gave 13 g (62 %) of pure (phenylthiomethyl)pentamethyldisilane (VI). A sample of this compound did react with bromine violently. Its IR spectrum exhibited no band near 1050 cm^{-1}

(8) With $(C_2H_5)_2NH$. In a sealed tube as above was heated a mixture of 15 g (0.083 mole) of (I) and 18.3 g (0.25 mole) of diethylamine at 95–110° for 54 h. At this point, we added 45 ml of 8% aqueous solution of sodium hydroxide to the reaction mixture in order to dissolve the precipitated salt. The organic layer was separated and fractionally distilled to give 10.5 g (79 % yield on the basis of unrecovered (I) of [(diethylamino)methyl]pentamethyldisilane (VII). A sample of this compound violently reacted with bromine. Its IR spectrum showed no band near 1050 cm^{-1}

(9) With $C_6H_5NH_2$. In a 100-ml flask, a mixture of 15 g (0.083 mole) of (I) and 24 g (0.25 mole) of aniline was heated with stirring at 100–130° for 21 h. To the mixture was then added 100 ml of 15 % aqueous solution of sodium hydroxide. Fractional distillation of the organic layer, separated and dried over calcium oxide, gave 7 g (36 % yield) of (anilinomethyl)pentamethyldisilane (VIII). The IR spectrum exhibited no band near 1050 cm^{-1} characteristic of the C–H deformation in the $SiCH_2Si$ group.

(10) With tert-C_4H_9ONa in tert-C_4H_9OH (attempted). In a sealed tube a mixture of 15 g (0.083 mole) of compound (I), 0.91 mole of sodium *tert*-butoxide and 15 ml of *tert*-butyl alcohol was heated at 95–110° over a period of 125 h. At this point all the starting substance (I) was recovered unchanged.

(11) With CH_3CO_2K in CH_3CO_2H. In a 100-ml flask we heated a mixture of 25 g (0.14 mole) of (I) and 17 g (0.17 mole) of fused potassium acetate in 25 ml of glacial acetic acid at 145° for 70 h. During the course of reaction, small samples were taken out from the mixture several times and analyzed by GLC. This analysis showed that a small amount of $(CH_3)_3SiSi(CH_3)_2CH_2O_2CCH_3$ (IX) appeared after 1 h, some quantity of $(CH_3)_3SiCH_2Si(CH_3)_2O_2CCH_3$ (X) had been formed after 20 h and the conversion to (X) was extensive after 70 h. Fractional distillation of the organic layer gave 14 g (50 % yield) of acetoxypentamethyldisilylmethane (X), 4 g of a mixture of (IX) and (X), and 2 g of $[(CH_3)_3SiCH_2Si(CH_3)_2]_2O$. b.p. 126°/21 mm. A sample of (X) did not react with bromine. Its IR spectrum exhibited a fairly intensive, broad band near 1050 cm^{-1}, possibly attributable to the overlap of two bands of the C–H deformation in $SiCH_2Si$ and the Si–O stretching vibration.

Preparation of (acetoxymethyl)pentamethyldisilane (IX)

A mixture of 5 g (0.03 mole) of (hydroxymethyl)pentamethyldisilane and 3.1 g (0.03 mole) of acetic anhydride was heated to reflux for 1 h. At this point the reaction was found to be complete by GLC. Fractional distillation gave 4.5 g (71 % yield) of (IX). A sample of this product did react with bromine violently. The IR spectrum showed no band near 1050 cm^{-1}, assignable to C–H deformation in $SiCH_2Si$ structure.

Preparation and attempted reaction with sodium alkoxides, of (methoxymethyl)pentamethyldisilane (XI)

To a stirred mixture of 13.1 g (0.54 g-atom) of magnesium, a small quantity of mercuric chloride and 30 g (0.18 mole) of chloropentamethyldisilane in 300 ml of THF was added dropwise (2 h) 43.5 g (0.54 mole) of monochloromethyl ether diluted with 100 ml of THF with external cooling. The reaction mixture was allowed to stand overnight. It was then decomposed with a saturated solution of ammonium chloride. The organic layer was separated, dried over potassium carbonate and fractionally distilled to give 14 g (44 % yield) of (methoxymethyl)pentamethyldisilane (XI). The IR spectrum of this compound exhibited a band at 1106 cm^{-1} characteristic of C–O stretching in ether structure, but no bands at 1050 (C–H deformation in $SiCH_2Si$) and at 1094 cm^{-1} (Si–O stretching). A sample of (XI) reacted with bromine violently. Another sample (0.5 ml) was heated to reflux in ethanol (2 ml) without undergoing any change for 8 h in the presence as well as absence of sodium ethoxide.

Reaction of (iodomethyl)pentamethyldisilane with silver oxide in methanol

To a stirred mixture of 12 g (0.044 mole) of (iodomethyl)pentamethyldisilane and 0.7 g (0.022 mole) of methanol was added 5.1 g (0.022 mole) of silver oxide in portions at room temperature. It was then heated at 60–70° for 3 h. GLC analysis of a sample from the reaction mixture indicated that the only product was $[(CH_3)_3SiCH_2Si(CH_3)_2]_2O$.

Preparation and cleavage of (cyanomethyl)pentamethyldisilane (XII)

To a stirred ether solution of 7.9 g (0.15 mole) of cyanogen was added dropwise a Grignard solution, prepared from 30 g (0.17 mole) of (chloromethyl)pentamethyldisilane (I), at −70° The reaction mixture was allowed to stand overnight and then hydrolyzed with a saturated solution of ammonium chloride. The organic layer combined with several ether extracts was fractionally distilled to give 15 g (53 % yield) of (cyanomethyl)-

pentamethyldisilane (XII). No band in its IR spectrum was shown near 1050 cm^{-1} A sample of (XII) was refluxed in ethanol for 13 h without undergoing any change. Addition of a catalytic amount of sodium cyanide to the reaction system, however, gave rise to a complete cleavage of the cyanomethyl group from silicon within 3 h to produce ethoxypentamethyldisilane and acetonitrile (identified by gas chromatography).

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CHAPTER SIX

PREPARATION OF CERTAIN BROMOMETHYL- AND IODOMETHYL-SUBSTITUTED DISILANES

SUMMARY

A very convenient route to bromomethyl-substituted organodisilanes involving reaction of the corresponding methoxymethyl disilanes with triphenyldibromophosphorane is described. Iodomethyl disilanes were best prepared by treatment of the bromomethyl disilanes with sodium iodide in acetone, although they could be made by the action of phosphoric acid and potassium iodide on the methoxymethyl disilanes, with yields and purities being much lower. 1,2-Bis(chloromethyl)tetramethyldisilane was prepared pure, but in very low yield, by the action of diazomethane on *sym*-dimethyltetrachlorodisilane followed by methylation of the remaining silicon-chlorine bonds.

INTRODUCTION

In the course of an extended investigation into the organofunctional disilanes and trisilanes[1-4], it became necessary to prepare several halomethyl-substituted disilanes such as $(XCH_2)Me_2SiSiMe_2(CH_2X)$ and $Me_3SiSiPhMe-(CH_2X)$, where X stands for a halogen atom. Many methods are available for making halomethyl silicon compounds[5], but none of them has turned out to be used satisfactorily for synthesis of relatively large quantities of such compounds.

A most satisfactory method for synthesis has been found to take

advantage of the recently discovered[6] cleavage of aliphatic ethers by triphenyldibromophosphorane to give high yields of alkyl bromides. This chapter is mainly concerned with the preparation of certain bromomethyl-substituted disilanes from the corresponding (methoxymethyl)disilanes by this new approach. Preparations of (iodomethyl)disilanes and 1,2-bis(chloromethyl)tetramethyldisilane are also described.

PREPARATIVE METHODS

Formulas, some physical properties and analytical data for the new compounds prepared in this study are listed in Table 1, and ^{1}H NMR data for some of them in Table 2.

(Bromomethyl)disilanes

The very convenient synthesis of (bromomethyl) pentamethyldisilane (I), 1,2-bis(bromomethyl)tetramethyldisilane (II), 1-(bromomethyl)-1-phenyltetramethyldisilane (III), and 1-(bromomethyl)-2-phenyltetramethyldisilane (IV) has been accomplished by the action of triphenyldibromophosphorane in chlorobenzene[6] on the corresponding (methoxymethyl)disilanes, *i.e.*, (methoxymethyl)pentamethyldisilane (V)[2], 1,2-bis(methoxymethyl)tetramethyldisilane (VI), 1-(methoxymethyl)-1-phenyltetramethyldisilane (VII) and 1-(methoxymethyl)-2-phenyltetramethyldisilane (VIII), respectively. The reaction conditions and yields are given in Table 3.

$$-\overset{|\ |}{\underset{|\ |}{Si}}SiCH_2OMe + Ph_3PBr_2 \xrightarrow[\text{reflux}]{\text{in } C_6H_5Cl} -\overset{|\ |}{\underset{|\ |}{Si}}SiCH_2Br + MeBr + Ph_3PO$$

It is interesting to note that (VI) is much more reactive than (V) toward the phosphorane reagent. Monitoring the progress of the reaction by GLC revealed that the former was consumed in 4 h, whilst the latter disappeared completely only after 20-h heating. (VII) and (VIII) were still less reactive, as seen from Table 3.

The (methoxymethyl)disilanes employed here were prepared by the known method which involves the reaction of the appropriate chlorodisilanes with chloromethyl methyl ether in the presence of magnesium in tetrahydrofuran[7,*] 1-Chloro-1-phenyltetramethyldisilane for synthesis of (VII) was prepared in 85% yield by aluminum chloride catalyzed chlorodephenylation of 1,1-diphenyltetramethyldisilane by hydrogen chloride in chloroform at room temperature[11] This reaction proceeded with cleavage of only one phenyl group.

$$Me_3SiSiMePh_2 + HCl \xrightarrow[\text{in } CHCl_3]{AlCl_3} Me_3SiSiMePhCl + PhH$$

Chlorodephenylation of (III) and (IV)

The silicon-phenyl bond in (III) and (IV) could readily be converted into the silicon-chlorine bond by treatment of these compounds with concentrated sulfuric acid in the cold and then with ammonium chloride. 1-(Bromomethyl)-1-chlorotetramethyldisilane (IX) (in 72% yield) and 1-(bromomethyl)-2-chlorotetramethyldisilane (X) (in 65% yield), respectively, were thus obtained.

$$Me_3SiSiMePh(CH_2Br) \xrightarrow[2.\ NH_4Cl]{1.\ H_2SO_4} Me_3SiSiMe(Cl)(CH_2Br) + PhH$$

(III) (IX)

$$PhMe_2SiSiMe_2(CH_2Br) \xrightarrow[2.\ NH_4Cl]{1.\ H_2SO_4} ClMe_2SiSiMe_2(CH_2Br) + PhH$$

(IV) (X)

* In place of magnesium, sodium[8] or lithium[9,10] may be used.

TABLE 1

Some Physical Constants and Analytical Data for New Compounds

Compound		B.p. (°C/mm)	n_D^{20}	d_4^{20}	MR_D Found	MR_D (Calcd.)	C % Found	C % (Calcd.)	H % Found	H % (Calcd.)
$C_6H_{17}BrSi_2$	(I)	57/9	1.4782	1.0849	58.81	(58.59)	32.07	(31.99)	7.36	(7.61)
$C_6H_{16}Br_2Si_2$	(II)	115/13	1.5257	1.4143	65.98	(66.31)	23.70	(23.69)	5.15	(5.30)
$C_{11}H_{19}BrSi_2$	(III)	95-96/1.5	1.5457	1.1527	78.90	(78.80)	46.19	(45.98)	6.62	(6.66)
$C_{11}H_{19}BrSi_2$	(IV)	98-100/1.5	1.5450	1.1526	78.83	(78.80)	45.99	(45.98)	6.74	(6.66)
$C_8H_{22}O_2Si_2$	(VI)	81/26	1.4432	0.8518	64.38	(64.04)	46.76	(46.54)	10.91	(10.74)
$C_{12}H_{22}OSi_2$	(VII)	108-109.5/10	1.5076	0.9154	77.61	(77.52)	60.08	(60.43)	9.24	(9.30)
$C_{12}H_{22}OSi_2$	(VIII)	83/2	1.5090	0.9149	77.83	(77.52)	60.53	(60.43)	9.36	(9.30)
$C_5H_{14}BrClSi_2$	(IX)	69-70/13[a]	------	------	----------		24.78	(24.44)	5.79	(5.74)[b]
$C_5H_{14}BrClSi_2$	(X)	98-99/33	1.4971	1.2429	57.86	(58.20)	24.82	(24.44)	6.15	(5.74)[c]
$C_6H_{16}I_2Si_2$	(XI)	103-105/1.5	1.5889	1.7451	76.88	(76.75)	17.95	(18.10)	4.19	(4.05)
$C_7H_{19}IOSi_2$	(XII)	104-106/14	1.5097	1.2744	70.91	(70.24)	28.28	(27.81)	6.60	(6.34)[d]
$C_6H_{16}Cl_2Si_2$	(XIII)	[e]	------	------	----------		33.67	(33.47)	7.56	(7.49)
$C_{10}H_{17}ClSi_2$[f]		117-118/20	1.5191	0.9802	70.90	(70.80)	52.44	(52.48)	7.60	(7.49)[g]

[a] M.p., 25-26°. [b] For the determination of halogen contents, see text. [c] Cl %: Found, 14.10; Calcd., 14.43.

[d] Slightly impure. [e] M.p., 37-39° [f] $Me_3SiSiMePhCl$. [g] Cl %: Found, 15.25; Calcd., 15.49.

(Iodomethyl)disilanes

The most frequently used procedure for cleaving ethers into iodides, which involves the use of either gaseous or aqueous hydrogen iodide, proved to be inapplicable to the synthesis of (iodomethyl)disilanes. No desired products were isolated at all. On the other hand, an application of the method reported by Stone and Shechter[12] to the methoxymethyl-substituted disilanes (V) and (VI), using excess orthophosphoric acid and potassium iodide as the ether cleaving reagent, afforded the expected (iodomethyl)-pentamethyldisilane[1] in 58% yield and 1,2-bis(iodomethyl)tetramethyldisilane (XI) in 30% yield. In the latter case, the reaction was incomplete under the conditions used and 1-(methoxymethyl)-2-(iodomethyl)tetramethyldisilane (XII) was also obtained in 18% yield.

$$-\overset{|}{\underset{|}{Si}}\overset{|}{\underset{|}{Si}}CH_2OMe + 2KI + 2H_3PO_4 \longrightarrow -\overset{|}{\underset{|}{Si}}\overset{|}{\underset{|}{Si}}CH_2I + MeI + 2KH_2PO_4 + H_2O$$

TABLE 2

^{1}H NMR Data for (Methoxymethyl)- and (Halomethyl)-disilanes, $RMe_2Si^{\beta}Si^{\alpha}MeR'(CH_2X)$ (τ values)[a]

Compound		$SiCH_3$		CH_2X	
		α	β		
(I)	$Me_3SiSiMe_2(CH_2Br)$	9.83	9.87	7.47	(X=Br)
(II)	$[(BrCH_2)Me_2Si-]_2$	9.72		7.42	(X=Br)
(III)	$Me_3SiSiMePh(CH_2Br)$[b]	9.53	9.86	7.28	(X=Br)
(IV)	$PhMe_2SiSiMe_2(CH_2Br)$[c]	9.86	9.61	7.53	(X=Br)
(V)	$Me_3SiSiMe_2(CH_2OCH_3)$	9.93[d]		6.90	(X=OMe)[e]
(VI)	$[(MeOCH_2)Me_2Si-]_2$	9.92		6.90	(X=OMe)[f]
(VII)	$Me_3SiSiMePh(CH_2OMe)$[g]	9.63	9.86	6.68	(X=OMe)[h]
(VIII)	$PhMe_2SiSiMe_2(CH_2OMe)$[i]	9.96	9.65	6.91	(X=OMe)[j]
(IX)	$Me_3SiSiMeCl(CH_2Br)$	9.42	9.76	7.30	(X=Br)
(X)	$ClMe_2SiSiMe_2(CH_2Br)$	9.75	9.48	7.42	(X=Br)
(XI)	$[(ICH_2)Me_2Si-]_2$	9.76		7.89	(X=I)
(XII)	$(MeOCH_2)Me_2Si^{\beta}Si^{\alpha}Me_2(CH_2I)$	9.83	9.87	7.91	(X=I)
				6.85	(X=OMe)[k]
(XIII)	$[(ClCH_2)Me_2Si-]_2$	9.82		7.10	(X=Cl)

[a] Measured on a JEOL Model C-60H in carbon tetrachloride. [b] Aromatic protons; 2.6-3. [c] Aromatic protons; 2.4-2.8. [d] Protons of five methyl groups appear in a single resonan [e] OCH_3; 6.73. [f] OCH_3; 6.73. [g] Aromatic protons; 2.4-2.8. [h] OCH_3; 6.74. [i] Aromatic protons; 2.4-2.9. [j] OCH_3; 6.73. [k] OCH_3; 6.71.

A more convenient preparative method of the (iodomethyl)disilanes comprises the action of sodium iodide on the (bromomethyl)disilanes in acetone[13] Thus (XI) could be obtained from (II) in a highly pure state and in substantially quantitative yield.

$$(BrCH_2)Me_2SiSiMe_2(CH_2Br) + 2NaI \longrightarrow (ICH_2)Me_2SiSiMe_2(CH_2I) + 2NaBr$$

(II) (XI)

In the course of this preparation we noticed by GLC analysis that the previously reported"1,2-bis(chloromethyl)tetramethyldisilane", which had been obtained through peroxide catalyzed chlorination of (chloromethyl) pentamethyldisilane with sulfuryl chloride[1], and also the"1,2-bis(iodomethyl)tetramethyldisilane" derived from it[1] were in fact a mixture of the respective 1,1- and 1,2-bis-(halomethyl) isomers. Comparison of the retention time on GLC of a pure sample of the 1,2-bis(iodomethyl)disilane (XI) here obtained with that of the previous sample showed that the isomer with a longer retention time corresponded to the 1,2-isomer.

TABLE 3

Preparation of (Bromomethyl)disilanes

Starting Material			Reaction Time[a]	Product		
No.	Weight (g)		(h)	No.	Weight (g)	Yield (%)[b]
(V)	17.6	(0.1 mole)	20	(I)	13.0	58
(VI)	10.3	(0.05 mole)	4	(II)	7.0	46
	33	(0.16 mole)	3		34.5	71
(VII)	23.9	(0.1 mole)	55	(III)	12.5	43.5
(VIII)	67	(0.28 mole)	24	(IV)	34	42

[a] At reflux temperature of the reaction mixture (*ca.* 130°). [b] Isolated yield.

(Chloromethyl)disilanes

In an effort to obtain a pure sample of 1,2-bis(chloromethyl)-tetramethyldisilane (XIII), we carried out the reaction of 1,2-dimethyltetrachlorodisilane with diazomethane by use of the techniques described in the literature[14-16] Although attempts to isolate the product in the form of *sym*-bis-(chloromethyl)dimethyldichlorodisilane were unsuccessful, subsequent treatment of the methylenation product with methylmagnesium bromide gave gas chromatographically homogeneous (XIII), though only in 3% yield.

$$Cl_2MeSiSiMeCl_2 + 2CH_2N_2 \longrightarrow$$

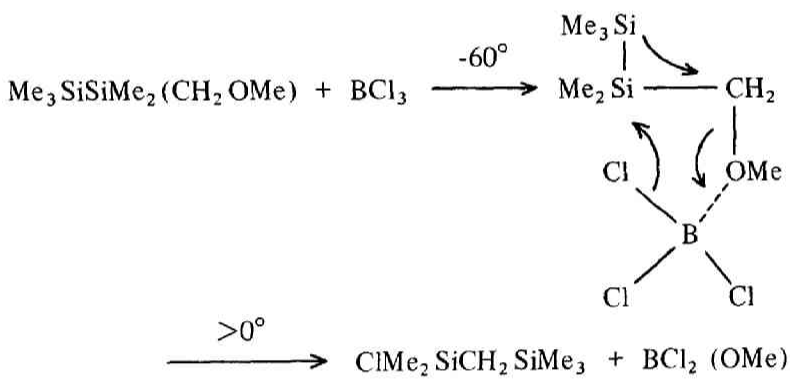
$$[(ClCH_2)ClMeSiSiMeCl(CH_2Cl)] + 2N_2$$

$$\downarrow MeMgBr$$

$$(ClCH_2)Me_2SiSiMe_2(CH_2Cl)$$

(XIII)

In order to learn whether it would be possible or not to transform the (methoxymethyl)disilanes into the corresponding (chloromethyl)disilanes, we treated (V) with boron trichloride[17] at -60° Immediately, a white crystalline mass believed to be an ether-boron chloride complex was formed. However, when it was allowed to warm up to room temperature it changed completely into (chlorodimethylsilyl)(trimethylsilyl)methane, probably *via* a mechanism as shown below.



EXPERIMENTAL

1-Chloro-1-phenyltetramethyldisilane

In a 300-ml three-necked flask, provided with an air-tight stirrer, a gas-inlet tube the stem of which extended into the liquid nearly the bottom of the flask, and a reflux condenser was placed a mixture of 182 g (0.65 mole) of 1,1-diphenyltetramethyldisilane[18], 450 ml of chloroform and 2.0 g of aluminum chloride. Into the stirred mixture was passed dry hydrogen chloride at room temperature, and the extent of the reaction was monitored by GLC analysis of small samples extracted periodically from the reaction mixture. After about 7 h, the starting substance disappeared with the formation of a

single product homogeneous by GLC. At that time the introduction of hydrogen chloride was discontinued and *ca.* 10 ml of acetone was added to the mixture for the purpose of deactivating the catalyst. Removal by distillation of the solvent and benzene produced as a result of reaction, followed by fractional distillation of the residue gave 126 g (85%) of 1-chloro-1-phenyltetramethyldisilane.

1,2-Bis(methoxymethyl)tetramethyldisilane (VI)

In a 2-l three-necked flask was placed a mixture of 62.2 g (2.56 g-atoms) of magnesium, a small amount of mercuric chloride, 60 g (0.32 mole) of 1,2-dichlorotetramethyldisilane[19] and 500 ml of dry tetrahydrofuran. To this mixture was added with stirring and external cooling in an ice bath a solution of 206 g (2.56 moles) of chloromethyl methyl ether in 300 ml of tetrahydrofuran. The reaction mixture was allowed to stand overnight, and then refluxed for 5 h. About 550 ml of the solvent was removed by distillation over a 4-h period, the mixture was decomposed with a saturated solution of ammonium chloride with cooling in an ice bath. The organic layer was separated, dried over potassium carbonate and fractionally distilled to give 33 g (50% yield) of 1,2-bis(methoxymethyl)tetramethyldisilane.

1-(Methoxymethyl)-1-phenyltetramethyldisilane (VII) and 1-(Methoxymethyl)-2-phenyltetramethyldisilane (VIII)

Similarly, (VII) was prepared in 67% yield from 1-chloro-1-phenyltetramethyldisilane and (VIII) in 73% yield from 1-chloro-2-phenyltetramethyldisilane[11]

(Bromomethyl)-substituted disilanes

The four (bromomethyl)-substituted disilanes (I)-(IV) were prepared in essentially the same manner. The following detailed description of the synthesis of (bromomethyl)-pentamethyldisilane (I) is typical.

In a 300-ml three-necked flask fitted with an air-tight stirrer, a dropping funnel and a reflux condenser, a suspension of triphenyldibromophosphorane was prepared by adding dropwise with cooling 17.6 g (0.11 mole) of bromine diluted with 20 ml of chlorobenzene to a solution of 28.8 g (0.11 mole) of triphenylphosphine in 100 ml of chlorobenzene[6] Disappearance of red color of bromine and precipitation of light yellow crystalline mass occurred immediately. To this mixture was added at a time, with stirring, a solution of 17.6 g (0.10 mole) of (methoxymethyl)pentamethyldisilane (V)[2] in 50 ml of chlorobenzene. The mixture was then heated to reflux with intermittent stirring for 20 h. The progress of the reaction was monitored by GLC. Most of the chlorobenzene was then removed by distillation under reduced pressure. To the residue in the flask was added *ca.* 250 ml of *n*-hexane and the precipitates (triphenylphosphine oxide) were filtered and washed with several small portions of *n*-hexane. The filtrate and washings were combined, washed with saturated $NaHCO_3$ solution and dried over $CaCl_2$. Fractional distillation gave the desired

product.

1-(Bromomethyl)-1-chlorotetramethyldisilane (IX)

To vigorously stirred 98 g (1.0 mole) of concentrated sulfuric acid was added dropwise 10.5 g (0.037 mole) of 1-(bromomethyl)-1-phenyltetramethyldisilane with external cooling in an ice bath over a 20-min period. After the addition was completed, the reaction mixture was stirred for an additional 1 h. To it was then added with cooling 17 g (0.32 mole) of ammonium chloride in several portions. The acid layer was extracted with about 60 ml of benzene and the extract was fractionally distilled to give 6.5 g (72% yield) of a crystalline product. Titration of an weighed sample with 0.1 N alkali under cooling with an ice bath gave a neutral equivalent (Found: 245 ; calcd.: 246) corresponding to the quantitative hydrolysis of only the Si-Cl bond, while back titration gave a neutral equivalent (Found: 124 ; calcd.: 123) corresponding to the total halogens (Cl plus Br).

1-(Bromomethyl)-2-chlorotetramethyldisilane (X)

In a similar manner to that above, 1-(bromomethyl)-2-phenyltetramethyldisilane was converted in 65% yield to 1-(bromomethyl)-2-chlorotetramethyldisilane.

(Iodomethyl)pentamethyldisilane

To a cooled mixture of 43.3 g of 95% phosphoric acid (0.42 mole as H_3PO_4) and 12.3 g (0.07 mole) of (methoxymethyl)pentamethyldisilane (V) was added 46.5 g (0.28 mole) of potassium iodide in several portions with stirring. The reaction mixture was allowed to stand at room temperature overnight and then heated at 90 $\pm$ 10° with vigorous stirring for 20 h. The progress of the reaction was monitored by GLC. The mixture was then hydrolyzed and the aqueous layer was extracted with 200 ml of ether. The organic layer and the extracts were combined and washed with sodium bicarbonate solution and then water, and dried over calcium chloride. Ether was removed by distillation and the remaining oil was fractionally distilled to give 11 g (58% yield) of (iodomethyl)pentamethyldisilane, b.p. 77-78°/11 mm[1]

1,2-Bis(iodomethyl)tetramethyldisilane (XI)

(a) In a similar manner to that above, 10.3 g (0.05 mole) of 1,2-bis(methoxymethyl)-tetramethyldisilane, 61.1 g of phosphoric acid and 66.5 g (0.40 mole) of potassium iodide were allowed to react, and the reaction mixture was worked up to give 2.7 g (18% yield) of slightly impure 1-(methoxymethyl)-2-(iodomethyl)tetramethyldisilane (XII), b.p. 104-106°/14 mm, and 6.0 g (30% yield) of 1,2-bis(iodomethyl)tetramethyldisilane (XI), b.p. 102-108°/1 mm, also in a slight pure state.

(b) A solution of 4.5 g (0.015 mole) of 1,2-bis(bromomethyl)tetramethyldisilane (II), and 5.6 g (0.037 mole) of sodium iodide in 60 ml of dry acetone was refluxed for

4 h. Since GLC analysis indicated that the reaction was complete at this point, acetone was removed by distillation and water was added to the residue. The organic layer and ether extracts from the aqueous layer were combined, washed with dilute sodium thiosulfate solution, then with water, and dried over potassium carbonate. Distillation gave very pure (XI) as a colorless liquid, in 93% yield.

1,2-Bis(chloromethyl)tetramethyldisilane (XIII)

In a 2-l three-necked flask, equipped with a stirrer, dropping funnel and reflux condenser the exit of which was protected by a drying tube, there was placed 34 g (0.15 mole) of *sym*-tetrachlorodimethyldisilane[20], 150 ml of absolute ether and 0.5 g of copper powder, prepared freshly from cupric chloride and zinc. To the mixture cooled to -30 to -40° in an acetone/Dry Ice-bath was added dropwise a solution of diazomethane (0.45 mole) in about 1.2 l of ether with vigorous stirring. During the addition, considerable deposition of a white mass (probably polymethylene) occurred on the vessel wall and catalyst surface and so an additional 2 g of copper powder was introduced in 0.5 g portions. The reaction mixture was stirred for 1.5 h at the same temperature and then allowed to stand overnight at room temperature. To the mixture was then added an ethereal solution of 0.8 mole of methylmagnesium bromide. The reaction mixture was worked up in the usual way. After removal of ether, the residue was flash-distilled to give 10 g of a liquid boiling over the range of 56-200°/23 mm, along with 5 g of residue. Fractional distillation of the distillate gave 2.9 g of impure (XIII), largely boiling at 111-120°/30 mm. Preparative GLC (180°, Apiezon-L, Varian Model 90P) from this fraction gave 1.2 g (3.1% yield) of the pure product. Several runs carried out in similar ways did not improve yields of the product.

Reaction of (methoxymethyl)pentamethyldisilane with boron trichloride

To 9 g (0.077 mole) of boron trichloride placed in a 50-ml three-necked flask, fitted with a Dry Ice-acetone condenser, gas inlet tube and serum cap, and cooled to -60° was added dropwise 8.8 g (0.05 mole) of (methoxymethyl)pentamethyldisilane[2] through the serum cap by means of a syringe. Immediately, the formation of white crystalline substance was observed, which was believed to be an ether-boron chloride complex because none of the reactants nor the product described below did not solidified under the same conditions. When the reaction mixture was allowed to warm to room temperature it turned clear. It was then stirred at room temperature for 2 h, during which period of time the progress of reaction was monitored by GLC. After standing overnight, the reaction mixture was distilled to give 8.8 g (98% yield) of (chlorodimethylsilyl)(trimethylsilyl)-methane, b.p. 84-86°/91 mm, n_D^{20} 1.4330 (reported[21]: b.p. 154-155°, n_D^{20} 1.4320)(Found: Cl, 20.08. $C_6H_{17}ClSi_2$ calcd.: Cl, 19.61%), along with 1 g a fore-run, boiling at 40-48° This major product did not react with bromine (evidence for the absence of the Si-Si bond) and its retention time on GLC coincided completely with that of an authentic sample.

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CHAPTER SEVEN

THE PREPARATION OF CERTAIN CHLOROMETHYL- AND DICHLOROMETHYL-SUBSTITUTED CHLORODISILANES AND THEIR BEHAVIOR TOWARD ALUMINUM HALIDES

SUMMARY

Four new chloromethyl disilanes, $(ClCH_2)Cl_2SiSiCl_2Me$ (I), $(Cl_2CH)Cl_2SiSiCl_2Me$ (II), $(ClCH_2)MeClSiSiClMe_2$ (III) and $(ClCH_2)Me_2SiSiCl_3$ (IV), have been prepared and studied as to their attitude toward intramolecular rearrangement with aluminum chloride. The reactivity decreases in the order : (III) > (IV) > (II) >> (I). Similar reactivity to rearrangement of $Me_3SiSiMe_2(CH_2Br)$ (V), $ClMe_2SiSiMe_2(CH_2Br)$ (VI) and $Me_3SiSiMeCl(CH_2Br)$ (VII) in the presence of aluminum bromide has been found to decrease in the order : (V) > (VI) > (VII). The results are discussed in terms of a mechanism favoring initial rate-determining step of ionization of the carbon-halogen bond in which the migrating group plays a minor role, if any, followed by migration of a silyl group from silicon to carbon. Disilanes (I) and (II) enter into the Friedel-Crafts reaction with benzene to give, after methylation, $PhCH_2SiMe_2SiMe_3$ and $Ph_2CHSiMe_2SiMe_3$, respectively.

INTRODUCTION

Kumada and his coworkers reported the preparation of (chloromethyl)- and (dichloromethyl)pentamethyldisilane through the photochemical chlorination of the "disilane fraction" of the methylchlorosilane distillation residue, followed

by treatment with a methyl Grignard reagent[1,2] However, intermediate chloromethyl derivatives that still contain chlorine atoms bonded to silicon could not be isolated in the pure state because the starting substance employed at that time was a rather complex mixture of methylchlorodisilanes of the general formula $Me_nSi_2Cl_{6-n}$. Recently, it has been reported that 1,2-dimethyltetrachlorodisilane could be prepared in the pure state very easily from the disilane fraction by treating it with acetyl chloride and anhydrous aluminum chloride at reflux temperature[3] The ready accessibility of this substance encouraged us to isolate 1-(chloromethyl)-2-methyltetrachlorodisilane (I) and 1-(dichloromethyl)-2-methyltetrachlorodisilane (II), and study some of their reactions. In this connection, we have prepared two further hitherto unknown chloromethyl-substituted chlorodisilanes, *i.e.*, 1-(chloromethyl)-1,2-dichlorotrimethyldisilane (III) and 2-(chloromethyl)-1,1,1-trichlorodimethyldisilane (IV), and examined the action of anhydrous aluminum chloride on all of them and also the action of anhydrous aluminum bromide on three (bromomethyl)disilanes (V)-(VII) described in Chapter 6.

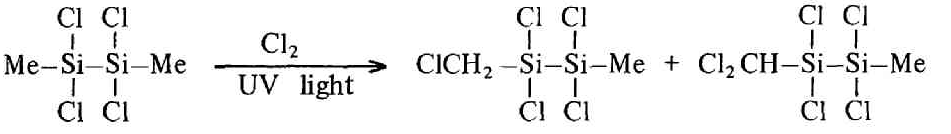
$Cl_2MeSiSiCl_2(CH_2Cl)$	(I)	$Me_3SiSiMe_2(CH_2Br)$	(V)
$Cl_2MeSiSiCl_2(CHCl_2)$	(II)	$ClMe_2SiSiMe_2(CH_2Br)$	(VI)
$ClMe_2SiSiMeCl(CH_2Cl)$	(III)	$Me_3SiSiMeCl(CH_2Br)$	(VII)
$Cl_3SiSiMe_2(CH_2Cl)$	(IV)		

Since the first work by Whitmore, Sommer and Gold[4], many papers have been devoted to the studies, particularly from a mechanistic point of view[5,6], of aluminum chloride-catalyzed intramolecular rearrangement of (chloromethyl)triorganosilanes, RMe_2SiCH_2Cl, R being an alkyl or aryl group, and (dichloromethyl)trimethylsilane, $Me_3SiCHCl_2$[7]. It has been well established that all of these compounds readily undergo rearrangement involving migration, from silicon to carbon, of a methyl or R group, depending upon the nature of R, but replacement of just one alkyl group on silicon by chlorine prevents the rearrangement (the compounds $Me_2ClSiCH_2Cl$ and $Me_2ClSiCHCl_2$ do not react with aluminum chloride[8]). Kumada *et al.* reported that the trimethylsilyl and chlorodimethylsilyl group in the (chloromethyl)disilanes $XMe_2SiSiMe_2(CH_2Cl)$, where X = Me or Cl, migrate much more readily than methyl groups to give

RESULTS AND DISCUSSION

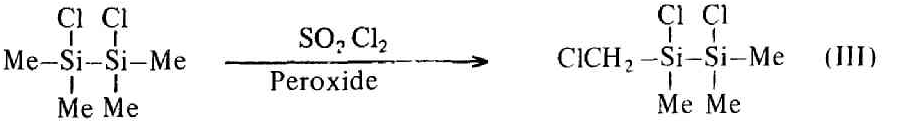
Preparation

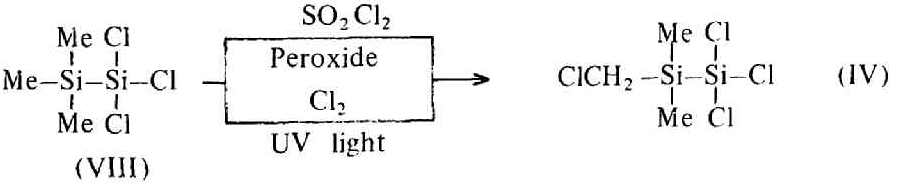
Photochemical chlorination of 1,2-dimethyltetrachlorodisilane[3] in the liquid phase followed by fractional distillation under reduced pressure gave very readily both (I) and (II):



(I) (II)

Peroxide-initiated chlorination with sulfuryl chloride of 1,2-dichlorotetramethyldisilane[9, 10] gave (III) in a satisfactory yield.





(VIII)

Compound (IV) was prepared in a similar way in 17% yield from 1,1,1-trimethyltrichlorodisilane (VIII), but photochemical chlorination of (VIII) in carbon tetrachloride proved to be more convenient and gave a better yield (31%). The trichlorotrimethyldisilane (VIII)[11] used here was prepared through aluminum chloride-catalyzed chlorodephenylation of 1,1,1-trimethyltriphenyldisilane[12] with dry hydrogen chloride in benzene.

The action of methylmagnesium bromide on (I) and (II) proceeded in the normal way and formed the known (chloromethyl)pentamethyldisilane[1, 2]

and (dichloromethyl)pentamethyldisilane[2] in 89 and 88% yield, respectively.

Some physical constants and ^1H NMR and analytical data for the chloromethyl-containing disilanes are listed in Table 1.

Titration of compounds (II) and (IV) with 0.1 N alkali at room temperature gave neutral equivalents corresponding to the quantitative hydrolysis of only the Si-Cl bonds. In striking contrast, titration of compound (I) gave a neutral equivalent corresponding to the total chlorine under the same conditions. With compound (III), only unreliable neutral equivalents were obtained upon titration at room temperature. However, titration with cooling in an ice bath gave the exact neutral equivalents corresponding to the Si-Cl bonds. Back titration of (III) after allowing it to stand with an excess of 0.1 N alkali for 50 h and then heating at 50° for 5 h gave the neutral equivalent corresponding to the total chlorine (see Table 1). The similar behavior was found for 1-(bromomethyl)-1-chlorotetramethyldisilane (VII), as mentioned in Chapter 6. The unusual reactivity of the carbon-halogen bond in these compounds will be discussed in the succeeding chapter.

TABLE 1

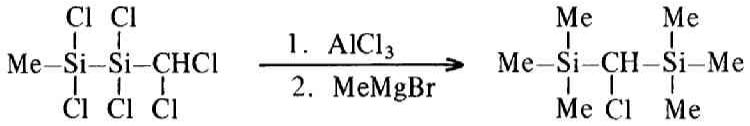
Physical Properties and NMR and Analytical Data for (Chloromethyl)disilanes

No.	Compound	B.p. (°C/mm)	(CH)[a] H^a	H^b	H^c	Chlorine(%) Found(Calcd.)	Silicon(%) Found(Calcd.)
I	$(CH_3^a)Cl_2SiSiCl_2(CH_2^cCl)$	80-84/19[b]	8.90		6.70	67.65 (67.53)[c]	21.83 (21.40)
II	$(CH_3^a)Cl_2SiSiCl_2(CH^cCl_2)$	100/16	8.86		4.45	47.44 (47.75)[d]	19.00(18.92)
III	$(CH_3^a)_2ClSiSi(CH_3^b)(Cl)(CH_2^cCl)$[e]	84-85/20	9.33	9.30	6.93	31.88 (31.99)[d] 47.12 (47.98)[c]	24.95(25.34)
IV	$Cl_3SiSi(CH_3^b)_2(CH_2^cCl)$[f]	86/21		9.51	6.99	44.48 (43.93)[d]	22.84(23.20)

[a] Spectra, determined in carbon tetrachloride, are given in ppm downfield from TMS at 60 Mc.
[b] M.p., 30-32° [c] Total chlorine content (see text). [d] Content of chlorine bonded only to silicon.
[e] Found: C, 22.65; H, 5.12. Calcd.: C, 21.67; H, 5.00%. [f] Found: C, 15.04; H, 3.40. Calcd.. C, 14.82; H, 3.31%.

Aluminum Halide-catalyzed Intramolecular Rearrangement

It was of interest to determine the relative ease with which compounds (I)-(IV) and (V)-(VII) undergo the aluminum halide-catalyzed intramolecular rearrangement involving migration of a silyl group from silicon to carbon. The extents of the rearrangement were estimated by GLC after methylation, *e.g.*,



The results are summarized in Tables 2 and 3.

A rapid redistribution of methylchlorodisilanes by the action of aluminum chloride has been observed[13] If such an undesirable reaction should occur in the present cases, comparison of the reactivity among these compounds toward the aluminum halide would become meaningless. GLC analysis of the reaction mixture of compounds (I), however, showed no such a redistribution reaction.

The data clearly show that the ease with which the rearrangement occurs falls in the order: (III)>(IV)>(II)>>(I), and (V)>(VI)>(VII). Thus it will well be said that, in general, the greater the total number of Si-Cl bonds in the molecule, the less readily the rearrangement takes place. Moreover, comparison of (VI) with (VII) on the one hand and (I) with (II) on the other, in either pair the total number of Si-Cl bonds being equal, reveals that a compound in which the silicon atom bearing a halomethyl group is less highly substituted by chlorine undergoes the rearrangement more easily than a compound having the similar silicon atom which is more highly substituted by chlorine, and that a compound having a dichloromethyl group is, other things being equal, more reactive than a compound having a chloromethyl group.

If we confine our consideration to the migratory aptitudes of the groups, it might be expected that they decrease in the order Me_3Si->$ClMe_2Si$->Cl_2MeSi->Cl_3Si-. The fact is that (IV) is more reactive than (I) on the one hand and (VI) rearranges more readily than (VII) on the other, and so it is very likely that the most important will be the stabilization, by electronic effects of substituents, of an incipient carbonium ion (or an electron-deficient

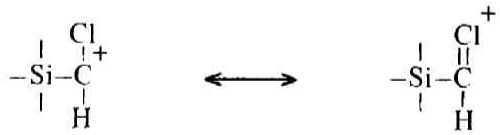
TABLE 2

The Action of Aluminum Chloride on Compounds (I)-(IV)[a]

Compound No.	Reaction conditions					
	20°		50°	80°		100°
	1 h	15 h	1 h	1 h	7 h	14 h
I					trace	trace
II					trace	21
III	trace	6	56	100		
IV	trace	trace	6	92		

[a] The extents of rearrangement are given in per cent.

transition state) brought about by complexation of the halomethyl group with the aluminum halide catalyst. Thus, the incipient carbonium ion (or the transition state) arising from compound (VI) is reasonably considered to be more strongly stabilized than that from compound (VII) and so the former undergoes the rearrangement more easily than the latter despite the migratory aptitude of $ClMe_2Si$- group is, other things being equal, smaller than that of Me_3Si- group. Further, the fact that (II) is much more reactive than (I) toward aluminum chloride may be explained in terms of the stabilization of the carbonium ion intermediate (or transition state) by an electromeric electron-donating effect of the chlorine atom directly bonded to it, as formulated below:



Analogously stabilized halocarbonium ions have been described by Olah *et al.*[14]

On the basis of kinetic studies on the aluminum chloride-catalyzed rearrangement of p-$XC_6H_4SiMe_2(CH_2Cl)$ (X = H, Me, and Cl) and Me_3SiCH_2Cl in 1,2-dichloroethane at -20°, Bott, Eaborn, and Rushton[5] proposed a mechanism involving synchronous intramolecular migration of the organic group and the

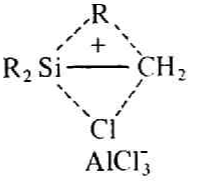
TABLE 3

Aluminum Bromide-Catalyzed Rearrangement of (V)-(VII)[a]

Compound[b] mole/l		$AlBr_3$ mole/l	Rearrangement (%) 1 min	10 min
$SiSiCH_2Br$	(V)			
0.146		0.032	99	
$ClSiSiCH_2Br$	(VI)			
0.153		0.045	91	96
$SiSiCH_2Br$ Cl	(VII)			
0.146		0.032	4	12
0.153		0.045	6	28

[a] In a benzene solution at 5° [b] For clarity, methyl groups are omitted.

chlorine atom (A). Thus, the rate-determining step involves the direct participation of the migrating organic group rather than the simple ionization of the C-Cl bond. Recently, Steward *et al.*[6] compared the migratory aptitudes of alkyl groups in (chloromethyl)trialkylsilanes under the action of aluminum



(A)

chloride and favored a two step mechanism involving an unstable intermediate (A), in which the first step involves heterolytic cleavage of the alkyl-Si bond and the second step the formation of the C-C bond.

For the rearrangement of (α-hydroxyalkyl)triphenylsilanes with boron trifluoride, Brook *et al.*[15] suggested a mechanism involving the initial formation

of the α-silylcarbonium ions and subsequent attack of fluoride ion on silicon and migration of phenyl group from silicon to carbon. Most recently, Hairston and O'Brien[16] followed the reaction of (α-haloalkyl)silanes with antimony pentafluoride by NMR and found the reaction to proceed stepwise; the initial ionization and subsequent rearrangement of the organic group from silicon to carbon.

From our results described above, it seems more likely that a mechanism for aluminum halide-catalyzed rearrangement of (halomethyl)disilanes involves initial slow, rate-determining step of ionization of the carbon-halogen bond where the migrating group plays a minor if any role, and subsequent, synchronous, fast step of nucleophilic attack of the halide ion on the silicon atom and migration of the silyl group from silicon to carbon.

Friedel-Crafts Reaction of (I) and (II) with Benzene

α- and β-Chloroethyltrichlorosilane and chloromethyltrichlorosilane have been shown to enter into the Friedel-Crafts reaction with benzene and its derivatives[17,18] An analogous reaction was found to occur between both (I) and (II) and benzene. Thus the reaction of (I) with benzene in the presence of aluminum chloride as catalyst at reflux temperature for 4 days, followed by treatment with methylmagnesium bromide gave 43% yield of benzylpentamethyldisilane (IX), whilst the reaction of (II) under similar conditions gave benzhydrylpentamethyldisilane (X) in 84.5% yield.

$$(I) + C_6H_6 \xrightarrow[2.\ MeMgBr]{1.\ AlCl_3} C_6H_5CH_2SiMe_2SiMe_3 \qquad (IX)$$

$$(II) + 2C_6H_6 \xrightarrow[2.\ MeMgBr]{1.\ AlCl_3} (C_6H_5)_2CHSiMe_2SiMe_3 \qquad (X)$$

Here again we find that (II) is much more reactive than (I).

EXPERIMENTAL

Photochlorination of 1,2-dimethyltetrachlorodisilane

1,2-Dimethyltetrachlorodisilane[3] (456 g; 2.0 mole) was chlorinated under irradiation of UV light, in essentially the same manner as reported previously[1] Fractional distillation of the reaction mixture under reduced pressure gave 85 g of compound (I) and 59 g of (II), along with 202 g of the unchanged starting material and 103 g of residue. Attempts to isolate any individual compound from the higher boiling material failed.

Methylation of (I) and (II)

The action of methylmagnesium bromide in ether on compound (I) (13.1 g; 50 mmole) followed by the usual work-up afforded 8 g (89% yield) of (chloromethyl)pentamethyldisilane[1,2] as a crystallizable material. Similarly, methylation of (II) (14.9 g; 50 mmole) gave 9.5 g (88%) of (dichloromethyl)pentamethyldisilane[1]

1-(Chloromethyl)-1,2-dichlorotrimethyldisilane (III)

In a 100-ml three-necked flask equipped with a reflux condenser, a stirrer and a pressure-equalizing addition funnel, was placed a solution of 40 g (0.214 mole) of 1,2-dichlorotetramethyldisilane[9,10] and 0.1 g of benzoyl peroxide. Sulfuryl chloride (43.5 g; 0.32 mole) was added to it with stirring at 80-85°C over a period of 0.5 h. After 3-h heating, a second portion of sulfuryl chloride (20 g; 0.15 mole) was added and then the mixture was heated for an additional 5 h. After flash distillation, fractionation through a short column packed with glass helices gave 11 g (23% yield) of (III), in addition to 14 g of the unchanged starting material.

2-(Chloromethyl)-1,1,1-trichlorodimethyldisilane (IV)

a) In essentially the same manner as described above, 46 g (0.22 mole) of 1,1,1-trichlorotrimethyldisilane (VIII) was treated with 61.2 g (0.45 mole) of sulfuryl chloride in the presence of 0.2 g of benzoyl peroxide. Fractional distillation gave 9 g (17% yield) of (IV) in the pure state.

b) Compound (VIII) (93 g; 0.4 mole) diluted with 100 ml of carbon tetrachloride was chlorinated by passing chlorine under irradiation of UV light in the usual manner[1] Without any external heating the reaction occurred. After a theoretical amount of hydrogen chloride was generated, the reaction mixture was distilled fractionally to give 30.5 g (31% yield) of (IV), together with 22.5 g of the unchanged starting material and 33 g of residue.

1,1,1-Trichlorotrimethyldisilane (VIII)

In a 1-l three-necked flask fitted with a gas-inlet tube, a stirrer and a reflux condenser the top of which was protected with a drying tube was placed a mixture of

280 g (0.84 mole) of 1,1,1-triphenyltrimethyldisilane[12], 800 ml of dry benzene and about 2 g of anhydrous aluminum chloride. Dry hydrogen chloride was passed through the stirred mixture at room temperature for 11 h. The extent of the reaction was followed by GLC analysis of small samples of the reaction mixture. Acetone (*ca.* 10 ml) was added to deactivate aluminum chloride. After filtration and removal of solvent, fractional distillation gave 132 g (75% yield) of (VIII) as a crystallizable material, b.p. 65-66°/40 mm, m.p. 23.5-24.5° (Found: C, 17.65; H, 4.26; Cl, 50.48. $C_3H_9Cl_3Si_2$ calcd.: C, 17.35; H, 4.37; Cl, 51.22%).

Action of aluminum chloride on (I) (IV)

A mixture of about 50 mg of a (chloromethyl)- or (dichloromethyl)chlorodisilane and a catalytic amount of anhydrous $AlCl_3$ was sealed in a small glass ampoule and maintained at a given temperature for a given period of time. After methylation of the reaction mixture with a methyl Grignard reagent, the extent of rearrangement was estimated by GLC by comparing an amount of $Me_3SiCH_2SiMe_3$ (or $Me_3SiCHClSiMe_3$) with that of (chloromethyl)pentamethyldisilane [or (dichloromethyl)pentamethyldisilane]. The results are listed in Table 2.

Action of aluminum bromide on (V) (VII)

A solution of bromomethyldisilane in benzene was placed in a well dried test tube and cooled to 5° A solution of aluminum bromide in benzene was then added at once. Small samples were extracted at suitable intervals and methylated with methylmagnesium bromide. The extents of rearrangement were estimated by GLC by comparing the amount of produced bis(trimethylsilyl)methane with that of nonane added as an internal standard.

The reaction conditions and the extents of rearrangement are listed in Table 3.

Reaction of compound (I) with benzene in the presence of $AlCl_3$

A mixture of 26.2 g (0.10 mole) of (I), 115 ml of dry benzene and 3.7 g of $AlCl_3$ was heated to reflux with stirring under a slow stream of dry nitrogen for 4 days. The reaction mixture was treated with a methyl Grignard reagent and worked up in the usual way. Fractional distillation through a short column gave 9.5 g (43% yield) of benzylpentamethyldisilane, b.p. 73-74°/2 mm, n_D^{20} 1.5080 (lit.[19] n_D^{20} 1.5092), along with 1.5 g of uncharacterized material, b.p. 134-135°/2 mm, n_D^{20} 1.5510, d_4^{20} 0.9484.

Reaction of compound (II) with benzene in the presence of $AlCl_3$

A mixture of 15 g (0.05 mole) of (II), 100 g of dry benzene and 2 g of anhydrous $AlCl_3$ was refluxed for 105 h and then worked up similarly. Distillation through a short Vigreux column gave 12.5 g (84.5% yield) of benzhydrylpentamethyldisilane, b.p. 136-137°/3 mm, n_D^{20} 1.5591, d_4^{20} 0.9626, MR_D Found 100.17, Calcd. 99.67 (Found:

C, 72.17; H, 8.62. $C_{18}H_{26}Si_2$ Calcd.: C, 72.40; H, 8.78%). NMR (τ values): $Si(CH_3)_3$, 10.12; $Si(CH_3)_2$, 9.90; $-CHPh_2$, 6.44; aromatic, 2.83.

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CHAPTER EIGHT

ALKALINE CLEAVAGE OF CERTAIN PHENYL- AND CHLORINE-SUBSTITUTED (HALOMETHYL)DISILANES

SUMMARY

The action of sodium ethoxide in ethanol on a number of (halomethyl)-disilanes containing phenyl groups or chlorine atoms on silicon has been studied. The reaction proceeds in three directions: intramolecular rearrangement involving migration of a silyl group from silicon to carbon, cleavage of the silicon-silicon bond with concomitant reduction of the halomethyl group to methyl, without evolution of hydrogen, and cleavage of the silicon-silicon bond with evolution of hydrogen. The rearrangement/cleavage proportions depend upon the nature and the position of the substituents. Possible mechanisms are discussed.

INTRODUCTION

In the preceding chapters 6 and 7, we described the preparation and some reactions of (halomethyl)disilanes containing grous(s) other than methyl on a silicon atom. The chemistry of such compounds, however, has received little attention so far, whereas a variety of reactions have been reported for monosilane analogs[1] It has been well recognized that a phenyl group in (chloromethyl)dimethylphenylsilane migrates from silicon to carbon under the influence of a sodium alkoxide in alcohol, affording finally a dimethyldialkoxysilane and toluene[2] We were interested in determining the

relative migratory aptitude of trimethylsilyl and phenyl group from silicon to carbon by base, and in elucidating the unusual high reactivity, upon titration with alkali, of the carbon-halogen bond in certain (halomethyl)disilanes, such as $Me_3SiSiMeCl(CH_2Br)$ (VII) (Chapter 6), $ClMe_2SiSiMeCl(CH_2Cl)$ (IX) (Chapter 7), and $Cl_2MeSiSiCl_2(CH_2Cl)$ (X) (Chapter 7). Therefore, we investigated the action of sodium ethoxide in ethanol on phenyl- and chlorine-substituted (halomethyl)disilanes.

As described in Chapter 5, the reaction of (halomethyl)disilanes with various nucleophilic reagents proceeds in five directions, depending upon the nature of the reagent used and of the nature and the position of substituents on silicon atom. Thus, with (chloromethyl)pentamethyldisilane, substitution of the chlorine atom exclusively takes place by sodium iodide in acetone[3], by sodium mercaptides in mercaptans or by amines (Course A)[4]; only silicon-carbon cleavage occurs with sodium (or potassium) cyanide in alcohols (Course B)[4]

$$Y^- + Me_5Si_2CH_2Cl \longrightarrow Me_5Si_2CH_2Y + Cl^- \qquad (A)$$

$$Y = I,\ C_2H_5S,\ C_6H_5S,\ Et_2N,\ C_6H_5NH$$

$$CN^- + Me_5Si_2CH_2Cl \xrightarrow{ROH} Me_5Si_2OR + CH_3CN + Cl^- \qquad (B)$$

With sodium alkoxides in alcohols, the reaction proceeds in three directions: intramolecular rearrangement of a silyl group from silicon to carbon (Course C)[3], cleavage of the silicon-silicon bond without evolution of hydrogen but with concomitant reduction of the halomethyl to methyl group (Course D), and cleavage of the silicon-silicon bond with evolution of hydrogen keeping the halomethyl group intact (Course E)*

In this chapter, our discussion is devoted primarily to the cleavage reactions (D) and (E).

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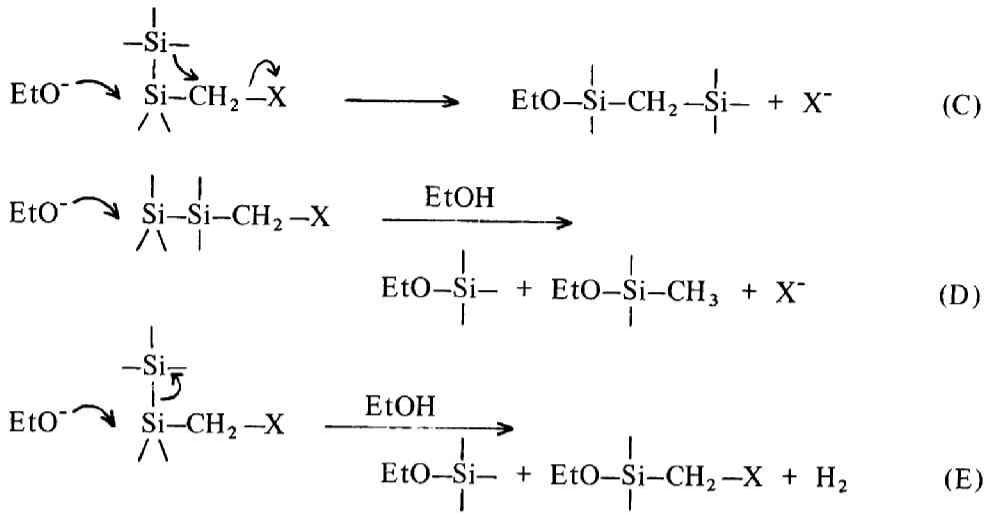
* The base-catalyzed cleavage of polysilanes with evolution of an equivalent of hydrogen for each silicon-silicon bond is well known[5]



RESULTS AND DISCUSSION

The reaction conditions, amounts of products determined by GLC and rearrangement/cleavage proportions are given in Table 1. The products were isolated by preparative GLC, after neutralization with dry hydrogen chloride, filtration and subsequent distillation, and identified mainly on the basis of IR and NMR spectra and elementary analyses.

In all cases examined, except only for compound (XI) whose reaction took Courses (C) and (E) (see below), no evolution of hydrogen occurred and the reaction proceeded according to Courses (C) and (D).

The above three modes of reaction, (C), (D) and (E), are represented in terms of synchronous processes, but such descriptions are intended for the sake of simplicity and not for any realistic mechanism; a two-step process may be more likely which involves a pentacovalent silicon intermediate being formed reversibly as a result of coordination by a nucleophile, followed by its decomposition in the rate-determining step to products[6] Which course the reaction preferentially takes may mainly depend on the substituents on the silicon atoms. The most important for determining the reaction course

may be the nature of a leaving anionic silyl group, although the relative concentration of the pentacovalent α- and β-silicon* intermediates in the prior equilibrium step will be none the less important.

(Halomethyl)pentamethyldisilanes

In Chapter 5, it has been described that the silicon-silicon bond in (chloromethyl)pentamethyldisilane (I) undergoes cleavage up to 30% with the chloromethyl group being reduced to methyl (Course D), in addition to 70% rearrangement (Course C). The analogous rearrangement and reduction of a halomethyl group were also found to occur with compounds (II) (Chapter 6) and (III)[3] In the series of (halomethyl)pentamethyldisilanes, $Me_3SiSiMe_2(CH_2X)$, (I) (III), the rearrangement/cleavage proportion increases in the order of X = Cl < I < Br, which is the same order as observed by Schott *et al.*[7] for the rearrangement/solvolysis ratio of (halomethyl)dimethylsilanes, HMe_2SiCH_2X (X = Cl, Br, I), under similar conditions. This may suggest that the rearrangement in both series proceeds by a similar mechanism.

Phenyl-substituted (halomethyl)disilanes

In marked contrast to (I) (III), 1-bromomethyl-1-phenyltetramethyldisilane (IV) (Chapter 6), under similar conditions, underwent cleavage up to 90% without evolution of hydrogen but with concomitant replacement of the bromine atom by hydrogen to give trimethylethoxysilane and ethoxydimethylphenylsilane, with the remaining 10% of the reaction proceeding *via* an intramolecular rearrangement to (ethoxymethylphenylsilyl)(trimethylsilyl)methane. An analogous result, (C) : (D)≃25 : 75, was obtained with 1-chloromethyl-1,2-diphenyltrimethyldisilane (VI). On the contrary, the reaction with 1-chloromethyl-2-phenyltetramethyldisilane (V) led to only about 26% cleavage, with 74% intramolecular rearrangement. This rearrangement/cleavage proportion is comparable to that for (chloromethyl)pentamethyldisilane, indicating that the reaction course is little affected by replacement of one methyl by a phenyl group on β-silicon.

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* The silicon atom bearing a halomethyl group is designated the α-silicon, and the other is the β-silicon.

TABLE 1

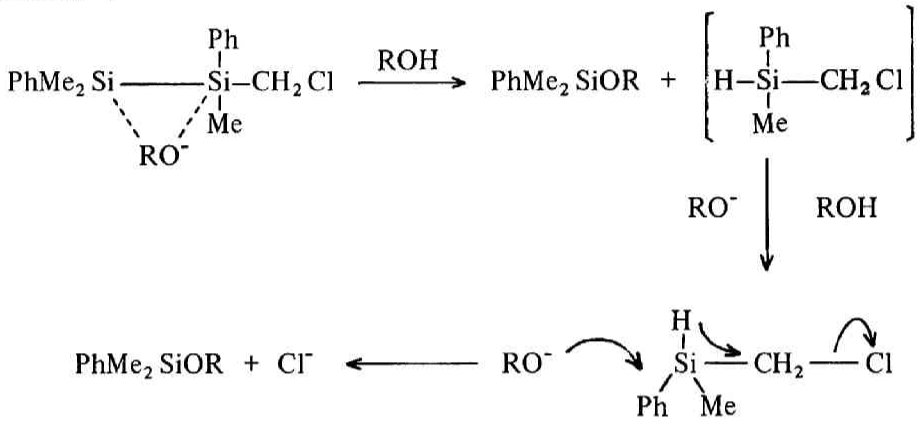
Reaction of (Halomethyl)disilanes with Sodium Ethoxide in Ethanol

No.	Compound	Reaction conditions		Products			Reaction proportions (%)[a]	
	mmole	Temp.	Time (h)[b]	Rearrangement mmole (yield %)	Cleavage mmole (yield %)		Rearrangement[c]	Cleavage[d]
I	$Me_3SiSiMe_2(CH_2Cl)$			$Me_3SiCH_2SiMe_2(OEt)$	Me_3SiOEt			
	30.0	r. t.	7 days[e]	11.4 (38)	8.6 (14)		73	27
		additional reflux	7 h	18.9 (63)	21.8 (36)		63	37
II	$Me_3SiSiMe_2(CH_2Br)$			$Me_3SiCH_2SiMe_2(OEt)$	Me_3SiOEt			
	5.1	r. t.	50	3.5 (68)	1.3 (13)		84	16
III	$Me_3SiSiMe_2(CH_2I)$			$Me_3SiCH_2SiMe_2(OEt)$	Me_3SiOEt			
	10.2	r. t.	50	5.3 (52)	5.2 (26)		67	33
IV	$Me_3SiSiMePh(CH_2Br)$			$Me_3SiCH_2SiMePh(OEt)$	Me_3SiOEt,	$PhMe_2SiOEt$		
	10.5	r. t.	1	0.91 (9)	8.66 (83)	9.5 (91)	10	90
V	$PhMe_2SiSiMe_2(CH_2Cl)$			$PhMe_2SiCH_2SiMe_2(OEt)$	Me_3SiOEt,	$PhMe_2SiOEt$		
	9.95	r. t.	26	6.64 (67)	1.53 (15)	2.25 (23)	73	26
VI	$PhMe_2SiSiMePh(CH_2Cl)$			$PhMe_2SiCH_2SiMePh(OEt)$	$PhMe_2SiOEt$			
	10.0	r. t.	20	2.30 (23)	13.6 (68)		25	75
VII	$Me_3SiSiMeCl(CH_2Br)$			$Me_3SiCH_2SiMe(OEt)_2$	Me_3SiOEt,	$Me_2Si(OEt)_2$		
	10.4	0°	5	9.5 (91)	0.3 (3)	0.3 (3)	97	3
VIII	$ClMe_2SiSiMe_2(CH_2Cl)$			$(EtO)Me_2SiCH_2SiMe_2(OEt)$	Me_3SiOEt,	$Me_2Si(OEt)_2$		
	9.9	0°-r. t.	24	1.75 (18)	5.9 (60)	3.9 (39)	23	77
IX	$ClMe_2SiSiMeCl(CH_2Cl)$			$(EtO)_2MeSiCH_2SiMe_2(OEt)$	$Me_2Si(OEt)_2$			
	9.9	0°-r. t.	50	9.1 (92)	2.2 (10)		90	10
X	$Cl_2MeSiSiCl_2(CH_2Cl)$			$(EtO)_3SiCH_2SiMe(OEt)_2$	$MeSi(OEt)_3$			
	10.8	0°	12	3.8 (36)	8.5 (40)		47	53
XI	$Cl_3SiSiMe_2(CH_2Cl)$			$(EtO)_3SiCH_2SiMe_2(OEt)$	$(EtO)_4Si$,	$(EtO)Me_2Si(CH_2Cl)$[f]		
	9.8	0°	1	2.9 (29)	7.2 (73)	6.8 (68)	28	72[g]

[a] The percentage adjusted to add to 100. [b] The time when GLC analysis was carried out; by that time the reaction had been complete. [c] Course (C). [d] Unless otherwise noted, Course (D). [e] Conversion, 55 %. [f] Hydrogen, 75%. [g] Course (E).

For the formation of $PhMe_2SiOEt$ from the cleavage of (IV) and (VI), one might conceive a pathway involving initial formation of hydride $HSiPhMe(CH_2X)$ as an intermediate, which subsequently undergoes nucleophilic intramolecular rearrangement involving the migration of hydrogen from silicon to carbon (Scheme 1).

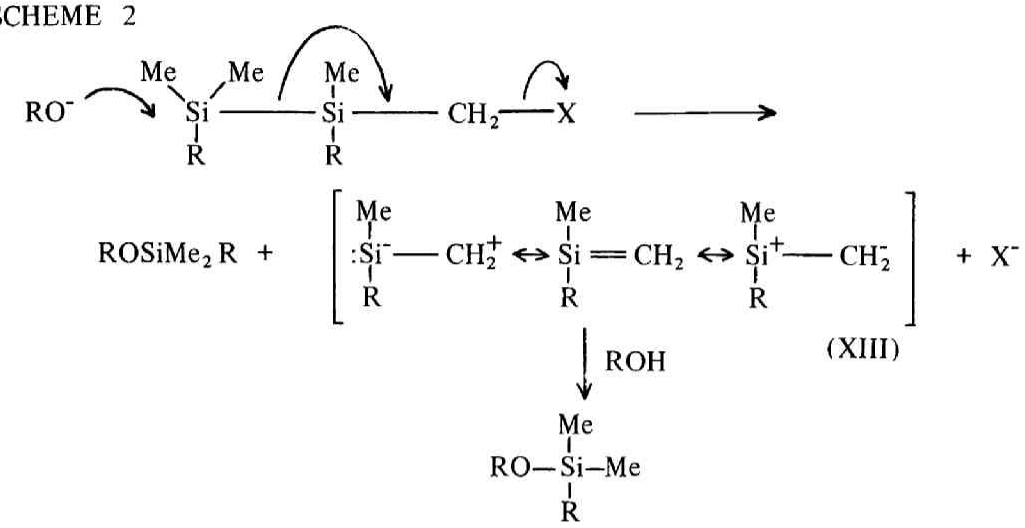
SCHEME 1



However, this can be ruled out, since evolution of hydrogen would result from the simultaneous ethanolysis of the silicon-hydrogen bond. Indeed, Sommer *et al.*[8] reported that the action of potassium hydroxide in 95% ethanol on (chloromethyl)dimethylsilane, HMe_2SiCH_2Cl, gave 31% of the silicon-hydrogen solvolysis product, $(HO)Me_2SiCH_2Cl$, with evolution of hydrogen, as well as 69% of the rearrangement product, Me_3SiOH. Similar results were described by Schott *et al.*[7] Further, we find that (chloromethyl)methylphenylsilane, $HPhMeSiCH_2Cl$, underwent 24% solvolysis with hydrogen evolution, in addition to 76% intramolecular rearrangement, on treatment with 2.2 M sodium ethoxide in ethanol at room temperature.

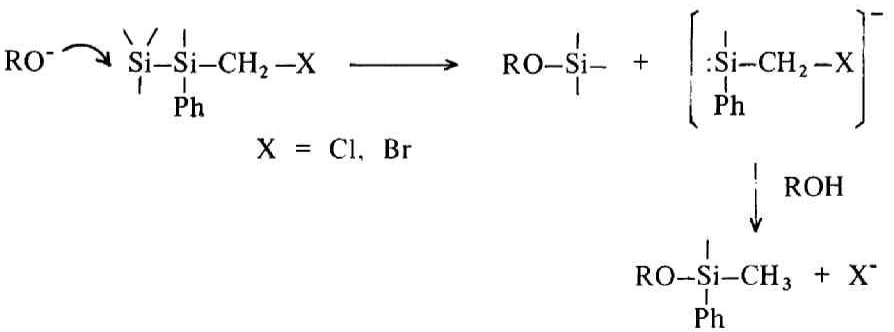
An alternative mechanism is synchronously proceeding β-elimination involving silicon[9] Thus, as the first step, an intermediate (XIII) is formed and solvent ethanol then adds to this unstable species to give the observed ethoxydimethylphenylsilane (Scheme 2).

SCHEME 2



Although several publications have recently appeared concerning the possible formation of methylenedimethylsilane, $Me_2Si{=}CH_2$, as an intermediate[10], a more acceptable mechanism would be described as a two step process rather than a synchronous "β-elimination" (Scheme 3). The first, probably rate-determining, step involves a nucleophilic substitution at the β-silicon atom, where the halomethylsilyl group as a whole is a leaving group. The presence of a phenyl group on the α-silicon atom may greatly favor the silicon-silicon cleavage of this type over the intramolecular rearrangement, possibly by stabilization of the leaving silyl anion[11] The second step is a rapid carbon-halogen bond breaking process with simultaneous addition of solvent ethanol, without intervention of such an intermediate species as (XIII).

SCHEME 3



Be that as it may, it can well be said that, unlike the intramolecular rearrangement (C) and the silicon-silicon cleavage with hydrogen evolution (E), the cleavage of the silicon-silicon bond with concomitant reduction of a halomethyl group proceeds by initial attack by an alkoxide ion on the β-silicon atom (D).

From the reaction of compound (IV) and (VI) bearing a phenyl group on α-silicon, no trace of toluene was detected by GLC, which might result from the migration of a phenyl group from silicon to carbon followed by cleavage of the silicon-benzyl bond by alkali[2] It follows that, under the influence of base, both trimethylsilyl and phenyldimethylsilyl groups migrate from silicon to carbon much more easily than does a phenyl group.

Chlorine-substituted (Halomethyl)disilanes

As mentioned in the preceding chapter, titration of $Cl_2MeSiSiCl_2(CH_2Cl)$ (X) with 0.1 N alkali at room temperature gives a neutral equivalent corresponding to the total chlorine content whereas other similar compounds such as $Cl_3SiSiMe_2(CH_2Cl)$ (XI) and $MeCl_2SiSiCl_2(CHCl_2)$ (XII) give neutral equivalents corresponding to the quantitative hydrolysis of only the Si-Cl bonds under the same conditions. This unusual reactivity of the C-Cl bond in (X) upon titration with base is reminiscent of the extremely facile cleavage of the C-Cl bond in (β-chloroethyl)trichlorosilane under the comparable conditions[12] The cleavage in the latter case has been formulated as a β-elimination involving silicon:

The formal analogy in unusual reactivity of the C-Cl bond between these two cases may suggest a resemblance of reaction mechanism and the base cleavage of the C-Cl bond in (X) to proceed according to Scheme 2 (apart from the problem of whether the realistic mechanism involves a synchronous, one-step or a two-step process). However, the C-Cl bond breaking in (X) by base may also, in part, be accounted for in terms of the nucleophilic intramolecular rearrangement. Indeed, the results, given in Table 1, of the

reaction of (X) and other related (halomethyl)disilanes indicate that all these compounds except for (XI) undergo, without evolution of hydrogen, both types of reaction, intramolecular rearrangement (C) and silicon-silicon cleavage with concomitant reduction of the halomethyl group (D), with the (C)/(D) proportion decreasing in the following order:

$$\underset{\text{(VII)}}{Me_3SiSiMeCl(CH_2Br)} > \underset{\text{(IX)}}{ClMe_2SiSiMeCl(CH_2Cl)} > \underset{\text{(II)}}{Me_3SiSiMe_2(CH_2Br)} >$$

$$\underset{\text{(III)}}{Me_3SiSiMe_2(CH_2\ I)} > \underset{\text{(I)}}{Me_3SiSiMe_2(CH_2Cl)} > \underset{\text{(X)}}{Cl_2MeSiSiCl_2(CH_2Cl)} >$$

$$\underset{\text{(VIII)}}{ClMe_2SiSiMe_2(CH_2Cl)}$$

It is very interesting to note that compound (VII) is most liable to the intramolecular rearrangement relative to the "elimination-type" cleavage on the one hand and the reverse is true for (VIII) on the other. A great difference in the value of the rearrangement/cleavage proportion between (VII) and (VIII) is much more than might be expected by considering the fact that the bromomethyl group favors intramolecular rearrangement over cleavage [compare the corresponding values for (I) and (II)]. Consequently, the difference in the position of chlorine attached to silicon between (VII) and (VIII) should be responsible for such a remarkable difference in the rearrangement/cleavage proportion value. Possibly, in the case of (VII) the attack of ethoxide ion on the α-silicon atom is favored over that on the β-silicon atom because an electronegative group (probably ethoxy group replaced for the original chlorine) is present apart from the halomethyl group, whilst the reverse is true for the case of (VIII) leading to displacement of $[:SiMe_2(CH_2Cl)]^-$ (not necessarily free but solvated), which is then rapidly converted into Me_3SiOEt and Cl^- Rather unexpectedly, a relatively high value of the rearrangement/cleavage proportion was obtained from the reaction of (X) with ethoxide ion although the α-silyl group would be considered to become a good leaving group while the β-silyl group a rather poor migrating group.

The C-Cl bond in $Cl_3SiSiMe_2(CH_2Cl)$ (XI) is, as described in the

preceding chapter, extremely stable under the conditions of alkaline titration. This can be ascribed to the fact that the X_3Si group (where X stands for Cl, OH and/or OR) is so good a leaving group relative to $SiMe_2(CH_2Cl)$ group and can be stabilized as an anion* that the attack of base will preferentially lead to the silicon-silicon cleavage (Course E) in the fashion depicted by Scheme 4. This view is supported by the observation that, upon treatment of (XI) with sodium ethoxide in ethanol, 75% of the theoretical amount of hydrogen was evolved and (chloromethyl)dimethylethoxysilane and tetraethoxysilane were formed in the amount corresponding to the gas evolution. The remaining part of the reaction took Course (C) to give (triethoxysilyl)(ethoxydimethylsilyl)methane and only traces of trimethylethoxysilane, expected from Course (D), were detected by GLC.

SCHEME 4

$$Cl_3SiSiMe_2(CH_2Cl) \xrightarrow{RO^-} [X_3Si:]^- + ROSiMe_2(CH_2Cl)$$

(XI)

$$[X_3Si:]^- \xrightarrow{2\ ROH} Si(OR)_4 + H_2 + RO^-$$

Under the conditions of alkaline titration, however, the reaction should proceed only *via* Course (E), because if Course (C) were also involved, titration would give an excess neutral equivalent over the quantity corresponding to the Si-Cl bonds only.

The fact that titration of 1-(dichloromethyl)-2-methyltetrachlorodisilane (XII) with alkali gives a neutral equivalent corresponding to the hydrolysis of only the Si-Cl bonds (Chapter 7), despite two chlorine atoms are bonded to the silicon atom bearing the dichloromethyl group, can be understood if one accepts that this group is cleaved as a whole from silicon by base to give dichloromethane[3, 14], which is unreactive to alkaline titration under the conditions used. Indeed, upon treatment with sodium ethoxide in ethanol,

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* A variety of characteristic reactions in which trichlorosilyl anion is believed to be involved are currently reported. See, *e.g.*, ref. 13.

(XII) gave methyltriethoxysilane, tetraethoxysilane and dichloromethane with evolution of an almost quantitative amount of hydrogen.

$$\underset{\text{(XII)}}{Cl_2MeSiSiCl_2(CHCl_2)} \xrightarrow[ROH]{RO^-} MeSi(OR)_3 + (RO)_4Si + CH_2Cl_2 + H_2$$

EXPERIMENTAL

NMR spectra were measured on a JEOL Model C-60H in carbon tetrachloride and the data are given in τ values. IR spectra were determined on a Hitachi Model EPI-G3 Grating Infrared Spectrophotometer.

1-Chloromethyl-2-phenyltetramethyldisilane (V)

To phenylmagnesium chloride (0.082 mole) in 100 ml of THF. 15.1 g (0.075 mole) of 1-chloromethyl-2-chlorotetramethyldisilane (VIII)[15] was added dropwise over a period of 40 min. The reaction mixture was heated to reflux with stirring for 10 h. After hydrolysis with a saturated solution of ammonium chloride, the organic layer was combined with the ether extracts from the aqueous layer, and dried over potassium carbonate. Flash distillation and subsequent fractionation gave 13 g (73% yield) of (V), b.p. 89-90°/4 mm, n_D^{20} 1.5321, d_4^{20} 0.9904, MR_D 76.01 (calcd. 76.17). (Found: C, 54.50; H, 7.84. $C_{11}H_{19}ClSi_2$ calcd.: C, 54.39; H, 7.88%.)

1-Chloromethyl-1,2-diphenyltrimethyldisilane (VI)

By a similar procedure to that described above, 35 g (0.155 mole) of 1-chloromethyl-1,2-dichlorotrimethyldisilane (Chapter 7) was reacted with excess phenylmagnesium chloride (0.50 mole) in 200 ml of THF After 10-h reflux and subsequent work-up, the organic layer was fractionally distilled to afford 38 g (81% yield) of (VI), b.p. 170-175°/4 mm, n_D^{20} 1.5806, d_4^{20} 1.0555, MR_D 96.24 (calcd. 96.11) (Found: C, 62.92; H, 6.73. $C_{16}H_{21}ClSi_2$ calcd.: C, 62.69; H, 6.94%.)

(Chloromethyl)methylphenylchlorosilane

A Grignard solution, prepared from 50 g (0.44 mole) of chlorobenzene and 12.2 g (0.50 g-atom) of magnesium in 300 ml of THF and filtered for the purpose of being free from excess magnesium, was added to a solution of 65.5 g (0.40 mole) of (chloromethyl)-methyldichlorosilane in 100 ml of THF at room temperature over a period of 30 min. Reflux for 2 h, removal of solvent and filtration were followed by distillation, which gave 55 g (67% yield) of (chloromethyl)methylphenylchlorosilane, b.p. 119-121°/17 mm (lit.[16] b.p. 136°/24 mm), n_D^{20} 1.5366, d_4^{20} 1.1798, MR_D 54.27 (calcd. 54.86).

(Chloromethyl)methylphenylsilane

To a suspension of 3.8 g (0.10 mole) of lithium aluminum hydride in 100 ml of ether was added dropwise a solution of (chloromethyl)methylphenylchlorosilane (20.5 g; 0.10 mole) in 50 ml of ether at room temperature with stirring over a period of 1 h. The mixture was then refluxed for 2 h and decomposed with water and then with *ca.* 5 N-hydrochloric acid. The organic layer and extracts from the aqueous layer were combined, washed with water and then dried over sodium sulfate. Fractionation gave, in addition to 4 g of phenyldimethylsilane, 9.5 g (56% yield) of (chloromethyl)methylphenylsilane, b.p. 97°/17 mm, n_D^{20} 1.5308, d_4^{20} 1.0449. MR_D 50.56 (calcd. 50.71) (Found: C, 56.48; H, 6.47. $C_8H_{11}ClSi$ calcd.: C, 56.25; H, 6.49%). NMR : 9.52 [d. SiCH_3 ; J(*H*Si-CH_3) 3.5 cps], 7.05 [d. CH_2Cl ; J(*H*Si-CH_2Cl) 3.0 cps], 5.47 (m. Si*H*), 2.35-2.85 (m. aromatic).

Reaction with sodium ethoxide in ethanol

General procedure: The reaction was carried out in a two-necked round-bottom flask, fitted with a serum cap and a condenser the top of which was connected to a gas buret for the purpose of measurements of the volume of hydrogen which might be evolved during the reaction. In the flask a solution of sodium ethoxide in ethanol was prepared by adding sodium or sodium ethoxide to ethanol. A (halomethyl)disilane was added through the serum cap by means of a syringe in the cold, except for (halomethyl)pentamethyldisilanes the reaction of which was carried out at room temperature. The reaction mixture was stirred magnetically for a given period of time. Dry hydrogen chloride was then passed through the reaction mixture in order to neutralize an excess of sodium ethoxide using phenolphthalein as an indicator. The yields of products (Table 1) were determined by GLC (at the outset, an appropriate hydrocarbon was added as an internal standard to the starting material). The identity of products was established as follows. The formed salt was filtered and the filtrate was flash-distilled under reduced pressure. Each product was isolated by fractional distillation or preparative GLC and identified on the basis of elemental analyses, IR and ^1H NMR spectra. On the infrared spectra, characteristic absorption bands near 1160 and 960 cm^{-1} for ethoxysilanes [17, 18], near 1050 cm^{-1} for the $SiCH_2Si$ structure assignable to the deformation vibration of the methylene group[19, 20] and in the region of 1050-1100 cm^{-1} due to the Si-O stretching vibration[18] were diagnostic of the identification of the reaction product.

The PEG-20M column packing (20% on Cerite, 8 ft., 60-70°) was the only one of the several tried that was effective for the satisfactory resolution of trimethylethoxysilane from ethanol.

Compound (I)–(III)

In addition to (ethoxydimethylsilyl)(trimethylsilyl)methane, which has been previously reported as an only product from the reaction of (I)[3], trimethylethoxysilane could be

isolated by preparative GLC and identified by comparison of its retention time on GLC and IR spectrum with those of an authentic sample.

Compound (IV)

To a solution of sodium ethoxide (75 mmole) in 40 ml of ethanol was added dropwise 14.4 g (50 mmole) of (IV) at room temperature with stirring. An exothermic reaction immediately occurred with white salt precipitating. After 1-h stirring, GLC analysis showed that the starting material was no longer present. No gas evolution was observed during the reaction. Trimethylethoxysilane and phenyldimethylethoxysilane were characterized by complete coincidence of retention times on GLC and IR spectra with those of authentic samples. A minor product was identified as (phenylmethylethoxysilyl)(trimethylsilyl)methane, n_D^{20} 1.4826 (Found: C, 61.86; H, 9.66. $C_{13}H_{24}OSi_2$ calcd.: C, 61.85; H, 9.58%.) NMR: 10.02 [s. $Si(CH_3)_3$], 9.96 (s. $SiCH_2Si$), 9.65 (s. $SiCH_3$), 8.85 (t. OCH_2CH_3), 6.38 (q. OCH_2CH_3), 2.35-2.9 (m. aromatic). GLC analysis of the reaction mixture did not show even traces of toluene.

Compound (V)

Reaction of 6 g (25 mmole) of (V) with sodium ethoxide (30 mmole) in 20 ml of ethanol at room temperature for 26 h formed trimethylethoxysilane and phenyldimethylethoxysilane, besides (phenyldimethylsilyl)(dimethylethoxysilyl)methane: n_D^{20} 1.4890, d_4^{20} 0.9199, MR_D 79.22 (calcd. 79.04) (Found: C, 62.70; H, 9.54. $C_{13}H_{2}OSi_2$ calcd.: C, 61.85; H, 9.58%.) NMR: 10.02 [s. $Si(CH_3)_2OEt$], 9.95 (s. $SiCH_2Si$), 9.70 [s. $Si(CH_3)_2Ph$], 8.87 (t. OCH_2CH_3), 6.44 (q. OCH_2CH_3), 2.35-2.9 (m. aromatic).

Compound (VI)

Similarly, 9.1 g (30 mmole) of (VI) was added to a solution of sodium ethoxide (45 mmole) in 25 ml of ethanol over 1 h. The mixture was then heated gently for ? h. Fractional distillation gave 5 g of phenyldimethylethoxysilane and preparative GLC afforded (phenylmethylethoxysilyl)(phenyldimethylsilyl)methane (Found: C, 68.71; H, 8.23. $C_{18}H_{26}OSi_2$ calcd.: C, 68.73; H, 8.23%). NMR: 9.71 (s. $SiCH_3$ and $SiCH_2Si$), 8.87 (t. OCH_2CH_3), 6.46 (q. OCH_2CH_3), 2.4-2.95 (m. aromatic).

(Chloromethyl)methylphenylsilane

With cooling in an ice bath, 5.4 g (31.6 mmole) of (chloromethyl)methylphenylsilane was reacted with 2.2M sodium ethoxide in ethanol (38 mmole). Immediate evolution of hydrogen resulted. After 20 min, the gas evolution ceased and 185 ml (at 20°) of hydrogen was collected, which indicates the occurrence of 24% solvolysis of the silicon-hydrogen bond. Work-up in the usual way followed by isolation by preparative GLC afforded, in addition to phenyldimethylethoxysilane, (chloromethyl)methylphenylethoxysilane, $(EtO)PhMeSiCH_2Cl$

(Found: C, 55.69; H, 7.17. $C_{10}H_{15}ClOSi$ calcd.: C, 55.92; H, 7.04%). NMR: 9.53 (s. $SiCH_3$), 8.80 (t. OCH_2CH_3), 7.11 (s. CH_2Cl), 6.24 (q. OCH_2CH_3), 2.3-2.9 (m. aromatic). None of methyltriethoxysilane and toluene, expected from migration of phenyl from silicon to carbon followed by cleavage of the silicon-carbon bond, was detected by GLC.

Compound (VII)

Reaction of 3.5 g (14.2 mmole) of (VII) with 34 mmole of sodium ethoxide in 40 ml of ethanol was carried out with cooling in an ice bath. Isolation by preparative GLC gave (diethoxymethylsilyl)(trimethylsilyl)methane, $(EtO)_2MeSiCH_2SiMe_3$ (Found: C, 48.04; H, 10.67. $C_9H_{24}O_2Si_2$ calcd.: C, 49.03; H, 10.97%). NMR: 10.23 (s. $SiCH_2Si$), 9.96 (s. $SiCH_3$), 8.82 (t. OCH_2CH_3), 6.27 (q. OCH_2CH_3). Trimethylethoxysilane and dimethyldiethoxysilane were identified by GLC.

Compound (VIII)

Compound (VIII) (2.0 g; 9.9 mmole) was treated with 30 mmole of sodium ethoxide in ethanol to form trimethylethoxysilane, dimethyldiethoxysilane and bis(ethoxydimethylsilyl)-methane. All the products were identified by GLC and IR spectra.

Compound (IX)

Treatment of 2.2 g (10 mmole) of (IX) with 40 mmole of sodium ethoxide in 50 ml of ethanol at 0° for 2 h and at room temperature for 10 h afforded dimethyldiethoxysilane and (diethoxymethylsilyl)(ethoxydimethylsilyl)methane, $(EtO)_2MeSiCH_2SiMe_2(OEt)$ (Found: C, 47.78; H, 10.34. $C_{10}H_{26}O_3Si_2$ calcd.: C, 47.95; H, 10.47%). NMR: 10.14 (s. $SiCH_2Si$), 9.95 (s. $SiCH_3$), 9.92 [s. $Si(CH_3)_2$], 8.87 (t. $SiOCH_2CH_3$), 8.83 [t. $Si(OCH_2CH_3)_2$], 6.40 (q. OCH_2CH_3), 6.31 [q. $(OCH_2CH_3)_2$].

Compound (X)

To a solution of sodium ethoxide (0.20 mole) in ethanol (150 ml) was added 6.6g (0.025 mole) of (X) in the cold over a 10-min period. After the addition was completed, the reaction mixture was stirred at room temperature for 5 h. No gas evolution was observed during the reaction. Neutralization, filtration and subsequent distillation gave a liquid boiling up to 115°/12 mm, which was collected in a flask cooled in an acetone-Dry Ice bath. Fractionation through a column packed with glass helices afforded 5.2 g of methyltriethoxysilane boiling at mainly 140-141°; n_D^{20} 1.3840 (lit.[21] b.p. 140-145°, n_D^{20} 1.3821), (Found: C, 47.05; H, 10.05. $C_7H_{18}O_3Si$ calcd.: C, 47.15; H, 10.18%).
The higher boiling product was isolated by preparative GLC and verified as (triethoxysilyl)-(diethoxymethylsilyl)methane, $(EtO)_3SiCH_2SiMe(OEt)_2$ (Found: C, 46.56; H, 9.82. $C_{12}H_{30}O_5Si_2$ calcd.: C, 46.42; H, 9.74%). NMR: 10.18 (s. $SiCH_2Si$), 9.92 (s. $SiCH_3$), 8.83 [t. $Si(OCH_2CH_3)_2$], 8.81 [t. $Si(OCH_2CH_3)_3$], 6.30 [q. $(OCH_2CH_3)_2$], 6.24 [q. $(OCH_2CH_3)_3$].

Compound (XI)

To a solution of 44 mmole of sodium ethoxide in 70 ml of ethanol was added 2.0 g (8.3 mmole) of compound (XI) with external cooling over a 3-min period. Immediately, a rapid evolution of hydrogen was observed. After 1-h stirring in the cold, the volume of hydrogen amounted to 143 ml (at STP), 75% of that expected if all the reaction proceeded *via* Scheme 4. The reaction mixture was then worked up and distilled to give a liquid boiling up to 125°/65 mm, consisting of three main products. They were isolated by preparative GLC, and identified as (chloromethyl)dimethylethoxysilane, tetraethoxysilane (by comparison of retention times on GLC and IR spectra with those of the authentic samples), and (triethoxysilyl)(ethoxydimethylsilyl)methane, $(EtO)_3SiCH_2SiMe_2(OEt)$ (Found: C, 46.33; H, 10.07. $C_{11}H_{28}O_4Si_2$ calcd.: C, 47.10; H, 10.17%). NMR: 10.17 (s. $SiCH_2Si$), 9.90 [s. $Si(CH_3)_2$], 8.86 (t. $SiOCH_2CH_3$), 8.81 [t. $Si(OCH_2CH_3)_3$], 6.40 (q. OCH_2CH_3), 6.25 [q. $(OCH_2CH_3)_3$].

Compound (XII)

A solution of 6.0 g (20.0 mmole) of (XII) in 5 ml of dry benzene was added to a solution of sodium ethoxide (140 mmole) in ethanol (70 ml) in the cold with stirring over 1 min. Immediately, rapid evolution of hydrogen occurred and ceased just after the addition had been completed and 385 ml at STP (17.2 mmole; 85%) of the gas was collected. Analysis of the reaction mixture by GLC showed the only formation of methyltriethoxysilane and tetraethoxysilane in the ratio of about 1 : 1, and dichloromethane.

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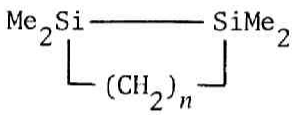
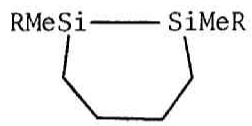
CONCLUSION

This thesis deals with the development of a new field of stereochemistry of cyclic organodisilanes in Part 1 and with the structure and reactivities of (halomethyl)disilanes in Part 2.

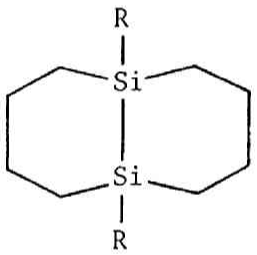
In Part 1, the preparation and stereochemistry of silicon-silicon-containing heterocyclic compounds, (A)–(D), have been described.



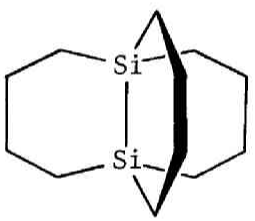
(A) n = 3 - 6



(B) R = p-XC_6H_4, F and Cl



(C) R = Me, Ph and Cl



(D)

The silicon-silicon bond involved in the five- and six-membered rings is substantially strained and more reactive than that in the acyclic analogs. Especially, the silicon-silicon bond in 1,1,2,2-tetramethyl-1,2-disilacyclopentane very easily reacts with sulfuric acid, alcoholic alkali and oxygen whereas this bond in the higher homologs and the open chain analogs is little affected under similar conditions. The geometrical isomers of 1,2-di-substituted-1,2-dimethyl-1,2-disilacyclohexanes (B) and 9,10-dimethyl-9,10-disiladecalin (C; R = Me) have been separated and characterized mainly on the basis of the dipole moment measurements, ^{1}H NMR spectra and/or stereospecific transformations from a compound of unknown configuration

to the other of known configuration. The stereochemical results of the silicon-silicon system obtained from the reactions using these cyclic compounds include: (a) the stereospecific oxidation of the silicon-silicon bond in *cis* and *trans* isomers of 1,2-diphenyl- and 1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane (B; R = Ph and F) and *cis* isomer of 9,10-dimethyl-9,10-disiladecalin (C; R = Me) with perbenzoic acid, bis(trimethylsilyl) peroxide and oxygen; (b) the complete stereomutation in the oxidation of *trans* isomer of (C; R = Me) with the peroxides; (c) the facile stereomutation of *cis* and *trans* isomers of (B; R = F) caused by alcohols in hydrocarbon; and (d) the stability of *cis*-9,10-disiladecalin over *trans* isomer. The tricyclic compound, 1,6-disila[4.4.4]propellane (D) has been prepared and in the course of its preparation strong evidence has been obtained for a silicon-magnesium compound to be formed as a fairly stable species.

In Part 2, mechanistic investigations into the reactions of (halomethyl)disilanes with nucleophilic and electrophilic reagents have been described. The reaction of (halomethyl)disilanes with various nucleophilic reagents proceeds in five directions, depending upon not only the nature of the reagent used but also the nature and the position of the substituents on silicon: (a) substitution of the halogen atom, (b) silicon-carbon cleavage, (c) intramolecular rearrangement of a silyl group from silicon to carbon, (d) cleavage of the silicon-silicon bond with concomitant reduction of the halomethyl group to methyl, without evolution of hydrogen, and (e) cleavage of the silicon-silicon bond with evolution of hydrogen keeping the halomethyl group intact. Furthermore, aluminum halide-catalyzed intramolecular rearrangement of chlorine-substituted (halomethyl)disilanes has been studied and the results suggest a mechanism favoring initial rate-determining step of ionization of the carbon-halogen bond.

In conclusion, it is briefly summarized that the *cis* and *trans* isomers of heterocyclic compounds containing the silicon-silicon bond and carbon chains are the most suitable materials to investigate the stereochemistry of the silicon-silicon bond and that the nature and the position of substituents on silicon change dramatically the reaction courses of cleavage of the silicon-silicon bond.

LIST OF PUBLICATIONS

Part One

Chapter 1 M. Kumada, K. Tamao, T. Takubo and M. Ishikawa, *J. Organometal. Chem.*, 9 (1967) 43.

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